Inorganica Chimica Acta, 54 (1981) L47–L49
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Ruthenium(II) Porphyrin Complexes: NMR Spectral Evidence for Out-of-Plane Ruthenium, and for Seven-Coordinate Species

G. DOMAZETIS, B. R. JAMES and D. DOLPHIN

Chemistry Department, University of British Columbia, Vancouver, British Columbia V6T 1Y6, Canada

Received January 29, 1981

Isolable ruthenium(II) porphyrin complexes with axial ligands are invariably six-coordinate, with the metal being essentially in the plane (within 0.1 Å) of the porphyrin ligand [1, 2]. Solution species have been studied by NMR, and data have been obtained on axial ligand exchange [3, 4] and ring-current contributions to chemical shifts [4, 5]; in addition, structural information may be obtained from a consideration or asymmetry in compounds of the type Ru(porp)(L_1)(L_2) [4]. For example, an anisochrony of the methylene protons within OEP* metalloporphyrins is induced by asymmetry introduced into the porphyrin ring either by having asymmetricallly coordinated ligands (five-coordinate geometry around the metal, or two different axial ligands) or by an asymmetrically coordinated (out of-plane) metal [6, 7]. The anisochrony (the diastereotopic protons having different chemical shifts) is readily detected by NMR as an ABX_3 pattern for the ethyl protons [6, 7].

We have studied ruthenium(II) porphyrins containing axial ligands [2, 9], and notice that bulky phosphine ligands produce significant asymmetry in Ru(OEP)(CO)(L) compounds; we report here data related to the coordination geometry and movement of the metal out of the porphyrin plane, which are germane to the potential catalytic activity of such complexes [8].

The syntheses of the complexes in the solid state or *in situ* via Ru(porp)(CO)(C_2H_5OH) precursors are described elsewhere [2, 8–10].

The ^1H NMR data for complexes 1–3, Table I, reveal asymmetry in the Bu^t_3 complex that is not present in the Bu^n_3P analogue; the methylene quartet in the t-butyl complex appears as a 10-line multiplet, similar to those observed in metal-out-of-the-plane porphyrin complexes [7, 8]. The ABX_3 pattern can be simulated by a system with J_{AB} = –16.1 Hz, J_{AX} = J_{BX} = 7.5 Hz. Exchange processes are ruled

TABLE I. ^1H NMR Spectra of Ruthenium(II) Porphyrin Complexes.[a]

Compound		OEP			Axial Ligands					
		Meso H	CH_2	CH_3	P–CH_2	P–C–CH_2	*o*-H	*m*-H	*p*-H	Others
1, Ru(OEP)(Bu^n_3P)$_2$		9.37(s)	3.88(q)	1.82(t)	–2.52(m)	–1.33(m)				0.5(m)
2, Ru(OEP)(CO)(Bu^n_3P)		9.94(s)	3.92(q)	1.92(t)	–2.91(m)	–1.68(m)				0.5(m)
3, Ru(OEP)(CO)(Bu^t_3P)		9.88(s)	A = 3.92 B = 4.10	X = 1.88(t)		–1.28(d)				
4 Ru(OEP)(np)$_2$		8.82(s)	3.65(q)	1.73(t)	–2.78(m)	–0.28(m)	3.92(m)	6.32(t)	6.65(t)	[b]
5 Ru(TPP)(np)$_2$[c]			[d]		–2.15(m)	+0.04(m)	4.29(m)	6.52(t)	6.84(t)	[e]
6 Ru(OEP)(CO)(np)[c]		9.55(s)	3.90(m)	1.87(t)	–2.97(m)	–0.30(m)	3.66(t)	6.36(t)	6.73(t)	[b]
7 Ru(OEP)(dpe)$_2$[c]	(i)	8.23(s)	3.65(q)	1.71(t)	–2.51(m)	–0.94(m)	3.81(m)			[f]
	(ii)	8.26(s)	3.56(m)	2.10(t)	–2.31(m)	–0.76(m)				
Ru(OEP)dpe)$_2$[g]		9.00(s)	3.70(q)	1.83(t)	–2.25(m)	–0.28(m)	4.00(m)	6.26(t)	6.54(t)	
8 Ru(OEP)(CO)(dpe)[h]	(i)	9.54(s)	3.86(q)	1.83(t)	–2.41(m)	–0.94(m)	3.56(6)	6.37(t)	7.18(m)	
	(ii)	8.87(s)	3.46(m?)	1.56(t)	–5.76(m)?	–1.0(m)?	2.71(t)	6.37(t)	6.78(m)	

[a] Chemical shifts in ppm relative to internal TMS [or external TMS with $CHCl_3$, (δ 7.25 ppm) or benzene (δ 7.15 ppm) as internal references] in $CDCl_3$ solution at 80 MHz; s = singlet, t = triplet, q = quartet, m = multiplet; [Ru] ~ 5 × 10^{-3} *M*. [b] 1.51(q), 0.19(t), due to uncoordinated –NEt_2. [c] Run at 400 MHz. [d] Pyrrole-H 8.09(s), porphyrin phenyls 7.59, 7.69(m). [e] 1.57(q), 0.27(t), due to uncoordinated –NEt_2. [f] Signals at 6.29(t),6.46(t), 6.67(t), 6.98(6), 7.0(t) and 7.31(s) are also observed. [g] In toluene-d_8. [h] *In situ* 1:1 Ru(OEP)(CO)(EtOH)/dpe; run at 270 MHz.

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*Abbreviations used: OEP and TPP = dianions of octaethylporphyrin and tetraphenylporphyrin, respectively; dpm = bis(diphenylphosphino)methane; dpe = 1,2-bis(diphenylphosphino)ethane; np = diethyl(diphenylphosphinoethyl)-amine, the np implying available N and P donor atoms.

TABLE II. Differences between Chemical Shifts (Δ ppm) of Free and Coordinated L Ligands in Ru(OEP)C(O)L) Complexes, and the Corresponding Distances (Å) calculated between the Porphyrin Plane and the Averaged Position of the Particular Proton (freely rotating).

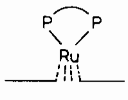
Ligand L		Δ (P–CH_2–) (Å)	Δ (P–C–CH_2–) (Å)	Δ (*o*-H)
Bu^n_3P (2)		4.28 (3.1)[a]	3.05 (3.6)[b]	
Bu^t_3P (3)		–	2.45 (4.8)[c]	
$Ph_2P(CH_2)_2NEt_2$ (6)		5.30 (2.6)a	2.80 (3.9)[b]	3.84 (3.5)
$Ph_2P(CH_2)_2PPh_2$ (8)	(i)	4.52 (3.0)a	3.07 (3.6)[b]	3.81 (3.6)
	(ii)	–	–	4.66 (3.1)

[a,b,c]The geometric distances calculated from models with Ru in the porphyrin plane are for *a* 2.8 ± 0.2 A, for *b* 3.6 ± 0.2 A, and for *c* 4.4 ± 0.1 A.

out by the invariance of the ^1H NMR in the absence and presence of excess phosphine, and by the ^{31}P shift of the coordinated phosphine which is identical at room temperature and –20 °C (66.1 ppm upfield to external $P(OMe)_3$). Calculations using Storm–Ellis models for ring current shifts of protons in axially coordinated ligands [4, 11, 12], Table II, suggest that in complex **3** the Ru is about 0.4 Å out of the plane towards the Bu^t_3P. A substantially lower ν(CO) value, 1912 cm^{-1} (KBr), compared with 1974 cm^{-1} for the Bu^n_3P complex **2**, indicates as expected much more effective metal-to-carbonyl π back-bonding when the metal is out of the porphyrin plane.

We have shown recently that the complex $Ru(TPP)(dpm)_2$ is six-coordinate in the solid state and solution, and contains monodentate diphosphines [2]. The ^1H NMR spectra of complexes **4–6** correspondingly reveal 'dangling' NEt_2 groups (Table I), but of interest the Ru(OEP)(CO)(np) complex, **6**, also shows the ABX_3 type spectrum (a multiplet at δ 3.90) typical of metal-out-of-the plane species. Storm–Ellis calculations using differences between shifts of free and coordinated $Ph_2P(CH_2)_2$ groups (Table II) provide some evidence for slight out-of-plane displacement of the ruthenium towards the np ligand; unfortunately, the computed distance is close to the error in the calculations. We are attempting to grow crystals of complexes **3** and **6** for an X-ray analysis in order to study any asymmetry in the metal geometry.

The ^{31}P data reported elswehere [2] for Ru(OEP)-$(dpe)_2$, 7, in the presence of excess dpe are again consistent with axial monodentate diphosphine ligands; however, in contrast to the dpm analogue [2], in the absence of added diphosphine in $CDCl_3$, dissociation of dpe occurs leading to complex ^{31}P spectra that vary with time, but low temperature data suggested the presence of species containing bidentate dpe [2]. The initial ^1H NMR of 7 in $CDCl_3$ (the meso-H and ethyl signals, Table I) shows two species, one giving again a complex pattern for the OEP methylene protons and being accompanied by a lower-field signal for the P–CH_2 protons consistent with them being a larger distance from the porphyrin. A species such as **I** seems plausible, but spectral changes over the time required for decoupling experiments prevents further confirmation. The much stronger tendency of dpe to chelate compared to dpm is well-documented [13]; however, the np ligand, which would give also the favoured five-membered ring, shows no such tendency judging by the ^1H NMR of complexes **4** and **5**. The ^1H NMR of 7 in toluene-d_8 (Table I, *g*) indicates just one species that resembles complex **4** containing dangling monodentate phosphines.



I

The ^{31}P and ^1H NMR spectra of a 1:1 Ru(OEP)-$(CO)(C_2H_5OH)$/dpe solution (**8**) are complex and are not simply due to a Ru(OEP)(CO)dpe) species with monodentate dpe (in contrast to the np

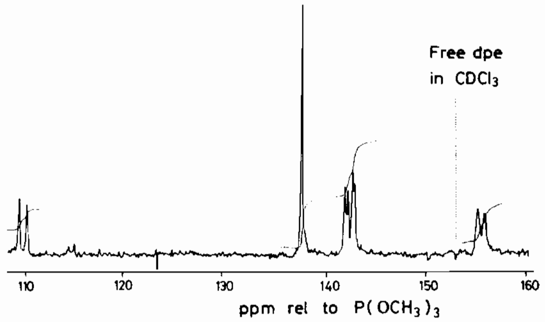
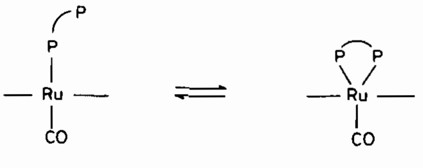


Fig. 1. ^{31}P NMR spectrum of an *in situ* $CDCl_3$ solution containing a 1:1 $Ru(OEP)(CO)(C_2H_5OH)$/dpe mixture at –20 °C; increasing ppm represents increasing field strength.

analogue 6). The ^{31}P spectrum at –20 °C is shown in Fig. 1. The singlet at 137.3 ppm is thought to result from a species containing a bridging dpe with equivalent phosphorus atoms, *e.g.* [Ru(OEP)(CO)]$_2$-dpe. The two sets of doublets (δ = 109.6, 141.9 ppm, J_{PP} = 32.1 Hz; δ = 142.2, 155.2 ppm, J_{PP} = 27.4 Hz) are tentatively attributed to an equilibrium between six- and seven-coordinate species;



(1)

II III

The ^{1}H NMR at room temperature shows two meso-H signals (Table I); one (δ 9.54 ppm) is very close to that observed for Ru(OEP)(CO)(np) and could be attributed to **II**, although the OEP methylene protons are not anisochronous in the dpe system. Evidence for **III** is provided perhaps by a large upfield shift of the *ortho*-protons of dpe (Table I, δ 2.71(t), assigned by decoupling of the *para*-protons). The chelate ring would force the phenyl groups closer to the porphyrin plane, leading to greater shielding. The small peak at δ –5.76 ppm may be the strongly shielded P–CH$_2$ protons.

Of interest, the solid state IR spectrum of Ru-(OEP(CO)(dpe) shows a major ν(CO) band at 1956 cm^{-1} and a minor peak at 1919 cm^{-1}, again consistent with an equilibrium such as (1). The major band is similar to the single one observed at 1958 cm^{-1} for Ru(OEP)(CO)(np) (corresponding possibly to **II**), while the smaller peak is close to that observed at 1912 cm^{-1} in the solid state for Ru(OEP)-(CO)(Bu$^t_3$P). A species such as **III** might be expected to have the ruthenium displaced towards the chelate ring with a resulting lowering of ν(CO). The NMR data are equivocal since the observed multiplet at δ 3.46 may be due to inequivalent methylene protons, or may be a quartet overlapping with other resonances.

In summary, these preliminary data indicate strongly that a) within six-coordinate porphyrin complexes, ruthenium may move out of the porphyrin plane, and b) seven-coordinate ruthenium porphyrins are feasible. We have no evidence as yet indicating out-of-the-plane ruthenium within the seven-coordinate species. Such considerations implying a potential vacant coordination site within six-coordinate ruthenium(II) porphyrin complexes, encourage us in our continued search [8] for organometallic-type homogeneous catalysis using such systems.

Acknowledgements

We thank the technical staff of this department for recording the NMR spectra, the National Sciences and Engineering Research Council of Canada and the U.S. Institutes of Health (AM 17989) for financial support, and Johnson, Matthey Ltd. for the loan of ruthenium. The work is a contribution from the Bioinorganic Chemistry group.

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