Inorganica Chimica Acta, *205* (1993) 137–143

Axial alkyl ligand reactivity in five-coordinate gallium(III) porphyrin complexes

Alan L. Balch*, Rebecca L. Hart and Sean Parkin

Department of Chemistry, University of California, Davis, CA 95616 (USA)

(Received July 27, 1992)

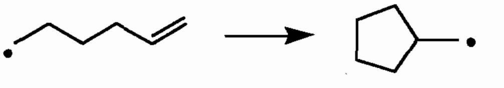
Abstract

Photochemical reactions of alkylgallium(III) complexes of tetraphenyl porphyrin dianion (TPP) have been monitored by ^{1}H NMR spectroscopy. Red–purple (TPP)Ga^{III}(cyclopentylmethyl)·$C_6H_5CH_3$, $C_{57}H_{47}N_4Ga$, crystallizes in triclinic space group $P\bar{1}$ with $a=10.877(3)$, $b=11.389(2)$, $c=18.786(3)$ Å, $\alpha=81.02(2)$, $\beta=11.389(2)$, $\gamma=74.36(2)°$ at 130 K with $Z=2$. Refinement of 477 parameters and 4616 reflections yielded $R=0.069$, $R_w=0.072$. The structure shows that the gallium ion is five-coordinate with the gallium 0.58 Å out of the N_4 plane. The Ga–C bond distance is 1.992(6) Å and the Ga–N distances span a narrow range from 2.095(4) to 2.110(3) Å. Photolysis of (TPP)Ga^{III}($(CH_2)_4CH=CH_2$) in benzene solution results in isomerization to form (TPP)Ga^{III}($CH_2CH(CH_2)_4$) as a result of homolysis of the Ga–C bond and cyclization of the 5-hexenyl radical. In the presence of dioxygen photolysis of (TPP)Ga$^{III}C_2H_5$ produces (TPP)Ga^{III}(OOC_2H_5) and photolysis of (TPP)Ga^{III}($(CH_2)_4CH=CH_2$) yields TPPGa^{III}($OO(CH_2)_4CH=CH_2$). In the latter case no isomerization (cyclization) to form TPPGa^{III}(($CH_2CH(CH_2)_4$) occurs because the 5-hexenyl radical is intercepted by dioxygen before it can cyclize. Nitrosobenzene (a radical trap) also inhibits isomerization (cyclization) of (TPP)Ga^{III}($(CH_2)_4CH=CH_2$).

Introduction**

Recently, it has been demonstrated that PFe^{III}R undergoes facile reactions with dioxygen at temperatures below −70 °C in toluene solution to form PFe^{III}OOR [1–3]. The same species can also be made by the addition of an alkyl hydroperoxide with PFe^{III}OH at low temperature [2, 4]. Because of their low thermal stability, these high-spin ($S=5/2$) five-coordinate peroxo complexes have been characterized primarily by ^{1}H and ^{2}H NMR spectroscopy below −70 °C. Corresponding chemistry is also seen with PGe$^{IV}R_2$ but photolysis at room temperature is necessary to activate the Ge–C bond which is otherwise unreactive toward dioxygen [5, 6]. That work allowed isolation of TPPGe$^{IV}(OOC_2H_5)_2$ and its structural characterization by X-ray crystallography [5].

Here, we examine the role of radical formation in the photochemical reactivity of another main group alkyl complex. For this we have used the gallium complexes (TPP)Ga^{III}R. Since these are five-coordinate and contain only a single axial ligand, their study avoids some of the complexity found in the germanium complexes, PGe$^{IV}R_2$, where the reactivity of two axial ligands must be considered [5]. In this work we have prepared complexes with both 5-hexenyl and cyclopentylmethyl axial ligands so that the well known cyclization of the 5-hexenyl radical (eqn. (1)) [7] could be used to monitor radical formation during photolysis.



(1)

The gallium complexes, PGa^{III}R, have been prepared previously [8] and their electrochemical behavior has been extensively studied [9, 10]. They are capable of forming six-coordinate complexes through the addition of a suitable base (*N*-methyl imidazole, pyridine) [10]. Addition of sulfur dioxide at −30 °C to PGa^{III}R produces PGa^{III}(SO_2R) in a non-photolytic reaction [11]. These sulfinato complexes are readily oxidized by dioxygen to give sulfanato complexes PGa^{III}(SO_3R). These exist as the O-bound isomers. The structure of (OEP)Ga^{III}(SO_3CH_3) has been determined by X-ray crystallography [11].

Results

Preparation and characterization of complexes

The alkylgallium(III) porphyrin complexes, which form green solutions, were prepared by standard means

---

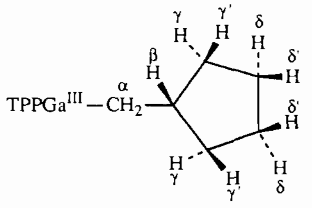
*Author to whom correspondence should be addressed.

**Abbreviations used: P, generic porphyrin dianion; TPP, tetraphenyl porphyrin dianion; OEP, octaethyl porphyrin dianion; R, alkyl group; THF, tetrahydrofuran.

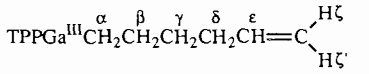
0020-1693/93/$6.00

through the addition of an appropriate Grignard reagent to (TPP)$Ga^{III}Cl$ [8, 9]. The alkoxy complexes, which give pink solutions, were obtained using procedures similar to those devised earlier for the preparation of (TPP)$Ga^{III}OH\cdot H_2O$ and (TPP)$Ga^{III}(O_2CCH_3)$ [10]. The resonances of the axial ligand substituents are quite characteristic since they are strongly shifted upfield by the porphyrin ring current. Relevant ^1H NMR data are given in Table 1. The ^1H NMR spectra also show pyrrole resonances at 9.10±0.5 ppm, *ortho* phenyl resonances (which generally appear as a doublet) at 7.45±0.10 ppm, and *meta* and *para* resonances as a broad multiplet at 7.45±0.10 ppm. Because they do not vary significantly from compound to compound, these porphyrin resonances are much less informative than the axial ligand resonances in Table 1. Figure 1 shows the ^1H NMR spectra for (TPP)$Ga^{III}((CH_2CH(CH_2)_4)$ (**1**) in trace A and (TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$ (**2**) in trace B. The resonance assignments to the various protons (labelled α to ζ) are made on the basis of chemical shift and spin–spin splitting. Those protons closest to the plane of the porphyrin are expected to show the strongest upfield shift.

1



2



$$\mathrm{TPPGa^{III}}\overset{\alpha}{\mathrm{CH_2}}\overset{\beta}{\mathrm{CH_2}}\overset{\gamma}{\mathrm{CH_2}}\overset{\delta}{\mathrm{CH_2}}\overset{\varepsilon}{\mathrm{CH}}{=}\mathrm{C}\genfrac{}{}{0pt}{}{\mathrm{H}\zeta}{\mathrm{H}\zeta'}$$

Notice that the α protons of the 5-hexenyl ligand appear as a triplet while those of the isomeric cyclopentylmethyl ligand appear as a doublet. Comparison of traces A and B reveals that the sample of **2** contains a small amount of the cyclized isomer **1**. This occurs because a small amount of cyclization accompanies the formation of the Grignard reagent [12, 13] used to form **2**.

Structure of (TPP)$Ga^{III}(CH_2CH(CH_2)_4)\cdot C_6H_5CH_3$

The structure of complex **1** has been determined by X-ray crystallography. A view of the complex is shown in Fig. 2. Atomic positional parameters are given in Table 2. Table 3 contains selected interatomic distances and angles. The asymmetric unit contains the five-coordinate complex with a toluene molecule occupying the space on the face of the porphyrin opposite the axial cyclopentamethyl ligand. There is a slight disorder in this structure. This results in a 90% occupancy of the gallium site shown in Fig. 2 and a 10% occupancy of a site (labelled Ga′ in Table 2) that is on the opposite face of the porphyrin. Only the major form is considered in Fig. 2 and Table 3. In the minor form the axial cyclopentamethyl ligand and the toluene molecule must have exchanged locations. However, the locations of the carbon atoms of the axial cyclopentamethyl group and the toluene molecule of the minor form are sufficiently close to that of the major form that it has not been possible to resolve any differences. This type of disorder is common among five-coordinate metalloporphyrins [14].

The Ga–N distances average 2.100 Å. This is longer than the average Ga–N distances seen in other five-coordinate gallium porphyrins: (OEP)$Ga^{III}(N_3)$ [15] Ga–N(av.) 2.035 Å; (OEP)$Ga^{III}(SO_3CH_3)$ [11] Ga–N(av.) 2.013 Å; (TPP)$Ga^{III}Cl$ [16] Ga–N(av.) 2.021 Å. The gallium ion is 0.58 Å out of the plane of the four porphyrin nitrogen atoms and 0.63 Å out of the plane of the entire porphyrin which is slightly saucer shaped. In this five-coordinate gallium complex, the Ga–C distance (1.992(6) Å) is at the long end of the range of Ga–C distances (1.936–1.990 Å) [17, 18] found in four- and three-coordinate gallium complexes. The porphyrin core and the cyclopentamethyl ligand show

TABLE 1. Axial ligand resonances[a, b] (ppm)

Compound	α	β	γ	δ	ζ	ζ'	ϵ
(TPP)$Ga^{III}(C_2H_5)$	−5.20(q) 2	−2.90(t) 3					
(TPP)$Ga^{III}(OC_2H_5)$	−0.90(q) 2	−1.60(t) 3					
(TPP)$Ga^{III}(OOC_2H_5)$	0.60(q) 2	−0.80(t) 3					
(TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$	−5.20(t) 2	−2.90(m) 2	−1.30(m) 2	0.58(q) 2	4.40(d) 1	4.53(d) 1	4.90(m) 1
(TPP)$Ga^{III}(O(CH_2)_4CH{=}CH_2)$	−1.10(t) 2	−1.44(m) 2	−0.75(m) 2	0.90(q) 2	4.53(d) 1	4.65(d) 1	5.16(m) 1
(TPP)$Ga^{III}(OO(CH_2)_4CH{=}CH_2)$	0.60(t) 2	−0.38(m) 2	0.05(m) 2	1.20(q) 2	4.60(d) 1	4.70(d) 1	5.28(m) 1
(TPP)$Ga^{III}(CH_2(C_5H_9))$	−5.00(d) 2	−2.40(m) 1	−1.90(m) 2	−0.85(m) 2	0.40(m) 4	0.40(m) 4	
(TPP)$Ga^{III}(OCH_2(C_5H_9))$	−1.15(d) 2	−0.99(m) 2	−0.92(m) 1	0.00(m) 2	0.72(m) 4	0.72(m) 4	
(TPP)Ga^{III}(OO-tBu)	−0.89(s) 9						

[a] Resonance multiplicity is given in parentheses: q, quartet; d, doublet; t, triplet; m, multiplet. This is followed by the relative intensity. [b] In benzene-d_6 at 23 °C.

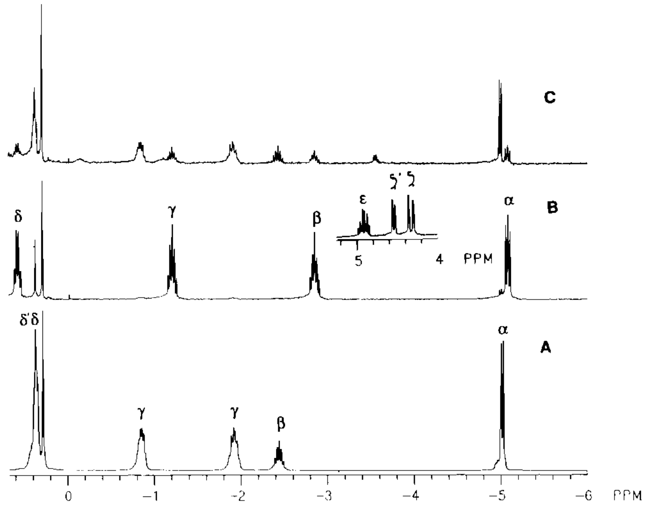


Fig. 1. ^1H NMR spectra benzene-d_6 solutions of: A, (TPP)$Ga^{III}(CH_2CH(CH_2)_4)$ (1); B, (TPP)$Ga^{III}((CH_2)_2CH{=}CH_2)$ (2); C, the same sample as B after photolysis for 1.5 h.

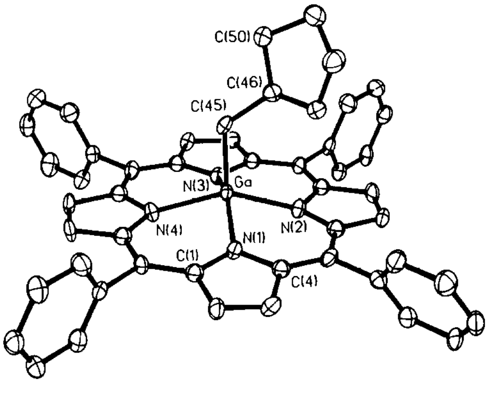


Fig. 2. A perspective drawing of (TPP)$Ga^{III}(CH_2CH(CH_2)_4)$ showing 50% thermal contours for all atoms. Only the major (90%) gallium location is shown, the minor (10%) site is not shown.

no unusual features except for some opening of the Ga–C(45)–C(46) angle (119.2(4)°). The widening of this angle is apparently necessary to accommodate the proximity of the cyclopentamethyl ligand and the porphyrin.

Photochemical isomerization of (TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$ (2) to (TPP)$Ga^{III}((CH_2CH(CH_2)_2)$ (1)

Photolysis of **2** in benzene results in isomerization to form **1**. Trace C of Fig. 1 shows the ^1H NMR spectrum of a sample of **2** in dioxygen-free, benzene-d_6 solution after photolysis for 1.5 h at 23 °C. Isomerization to form **1** has occurred as is readily seen by comparison with traces A and B. Integration versus a standard indicates that the yield of isomerized **1** is 37%.

When (TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$ is photolyzed in the presence of nitrosobenzene, a radical trap, no

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^3$)

	x	y	z	U_{eq}[a]
Ga	3171(1)	7361(1)	2182(1)	18(1)
Ga′	3397(4)	7596(4)	2833(4)	44(3)
N(1)	1754(3)	6846(3)	3012(2)	22(2)
N(2)	2115(3)	9168(3)	2312(2)	23(2)
N(3)	4795(3)	8089(3)	1917(2)	22(2)
N(4)	4439(3)	5764(3)	2590(2)	23(2)
C(1)	1807(4)	5688(3)	3372(3)	22(1)
C(2)	575(4)	5657(4)	3798(3)	27(2)
C(3)	−209(5)	6787(4)	3693(3)	28(2)
C(4)	517(4)	7541(3)	3196(3)	22(1)
C(5)	59(4)	8780(3)	2976(3)	23(2)
C(6)	807(4)	9530(4)	2558(3)	24(1)
C(7)	335(4)	10810(4)	2320(3)	25(2)
C(8)	1349(4)	11217(4)	1944(3)	27(2)
C(9)	2465(4)	10195(4)	1929(3)	22(1)
C(10)	3705(3)	10258(3)	1606(3)	23(2)
C(11)	4789(4)	9272(3)	1604(3)	22(1)
C(12)	6071(4)	9337(4)	1274(3)	25(2)
C(13)	6848(4)	8208(4)	1378(3)	25(2)
C(14)	6056(4)	7424(3)	1775(3)	23(1)
C(15)	6508(4)	6171(3)	1967(3)	24(2)
C(16)	5748(4)	5404(4)	2355(3)	23(1)
C(17)	6227(4)	4127(4)	2597(3)	27(2)
C(18)	5216(4)	3720(4)	2978(3)	29(2)
C(19)	4100(4)	4738(4)	2981(3)	23(1)
C(20)	2871(3)	4685(3)	3339(3)	23(2)
C(22)	−2278(3)	9009(3)	2912(2)	31(2)
C(23)	−3589	9536	3116	36(2)
C(24)	−3977	10412	3610	34(2)
C(25)	−3055	10761	3898	34(2)
C(26)	−1744	10234	3693	29(2)
C(21)	−1355	9358	3200	23(2)
C(28)	3632(3)	11828(3)	505(2)	34(2)
C(29)	3722	12984	156	35(2)
C(30)	4057	13798	523	30(2)
C(31)	4303	13457	1239	31(2)
C(32)	4214	12302	1588	28(2)
C(27)	3879	11487	1220	24(2)
C(34)	8369(3)	4935(3)	1154(2)	36(2)
C(35)	9689	4437	956	39(2)
C(36)	10569	4589	1366	34(2)
C(37)	10131	5239	1973	38(2)
C(38)	8812	5737	2171	31(2)
C(33)	7931	5585	1762	22(2)
C(40)	2299(3)	2675(3)	3371(1)	31(2)
C(41)	2184	1526	3719	37(2)
C(42)	2468	1161	4426	32(2)
C(43)	2867	1944	4785	33(2)
C(44)	2983	3093	4437	31(2)
C(39)	2699	3458	3730	24(2)
C(45)	2973(5)	6926(5)	1230(3)	21(2)
C(46)	2291(5)	7919(5)	697(3)	26(2)
C(47)	821(5)	8358(6)	923(3)	33(2)
C(48)	192(5)	8234(6)	287(3)	37(3)
C(49)	1239(5)	8255(6)	−377(3)	38(3)
C(50)	2438(6)	7513(6)	−58(3)	39(3)
C(2S)	3502(4)	6289(4)	5233(3)	59(4)
C(3S)	2374	6227	5718	69(4)
C(4S)	1192	6999	5573	69(4)
C(5S)	1139	7831	4943	84(5)
C(6S)	2267	7892	4459	75(5)
C(1S)	3449	7121	4604	50(3)
C(7S)	4650(11)	7242(10)	4080(5)	97(6)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Selected interatomic distances and angles in (TPP)Ga($CH_2CH(CH_2)_4$)·$C_6H_5CH_3$

Distances (Å)			
Ga–N(1)	2.110(3)	Ga–N(2)	2.096(3)
Ga–N(3)	2.095(4)	Ga–N(4)	2.099(3)
Ga–C(45)	1.992(6)		
C(45)–C(46)	1.519(7)	C(46)–C(47)	1.539(6)
C(46)–C(50)	1.527(8)	C(47)–C(48)	1.525(9)
C(48)–C(49)	1.524(7)	C(49)–C(50)	1.521(8)
Angles (°)			
N(1)–Ga–N(2)	85.6(1)	N(1)–Ga–N(3)	146.8(2)
N(2)–Ga–N(3)	85.5(1)	N(1)–Ga–N(4)	85.6(1)
N(2)–Ga–N(4)	148.1(2)	N(3)–Ga–N(4)	85.4(1)
N(1)–Ga–C(45)	109.9(2)	N(2)–Ga–C(45)	109.5(2)
N(3)–Ga–C(45)	103.2(2)	N(4)–Ga–C(45)	102.3(2)
Ga–C(45)–C(46)	119.2(4)	C(45)–C(46)–C(47)	114.7(4)
C(45)–C(46)–C(50)	113.1(4)	C(47)–C(46)–C(50)	104.1(5)
C(46)–C(47)–C(48)	107.0(4)	C(47)–C(48)–C(49)	104.7(5)
C(48)–C(49)–C(50)	101.4(4)	C(46)–C(50)–C(49)	105.8(4)

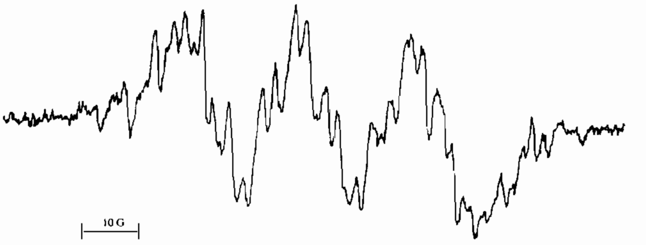


Fig. 3. The ESR spectrum obtained after photolysis of a benzene solution of (TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$ (**2**) and nitrosobenzene for 2 h.

cyclization to form **1** is observed in ^1H NMR measurements. However, the formation of a stable radical has been observed by electron spin resonance spectroscopy (ESR). Figure 3 shows the ESR spectrum of a solution of (TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$ and nitrosobenzene after irradiation for 2 h. The spectrum is typical for a nitroxide Ph(R)NO$^{\bullet}$.

Photolysis of (TPP)Ga^{III}R in the presence of dioxygen forms (TPP)Ga^{III}(OOR)

Figure 4 shows the results of photolysis of a sample of $TPPGaC_2H_5$ in benzene under one atmosphere of dioxygen. Trace A shows a portion of the spectrum of (TPP)$Ga^{III}(C_2H_5)$ before photolysis. Trace B shows the spectrum of the same sample after 1.5 h of photolysis. At this point a significant quantity of (TPP)$Ga^{III}(C_2H_5)$ remains. New resonances at 0.60 and −0.80 ppm indicate the presence of a new species with another axial ligand. These are identified as belonging to (TPP)$Ga^{III}(OOC_2H_5)$. Identical resonances are obtained when ethylhydroperoxide is added to (TPP)$Ga^{III}OH \cdot H_2O$. The axial ligand resonances of (TPP)$Ga^{III}(OC_2H_5)$ are clearly different. Other products whose resonances are seen in trace B include acetaldehyde and ethanol. These products apparently arise from photolysis (TPP)$Ga^{III}(OOC_2H_5)$, since the same products have been observed to form upon photolysis of (TPP)$Ge^{IV}(OOC_2H_5)_2$ [5].

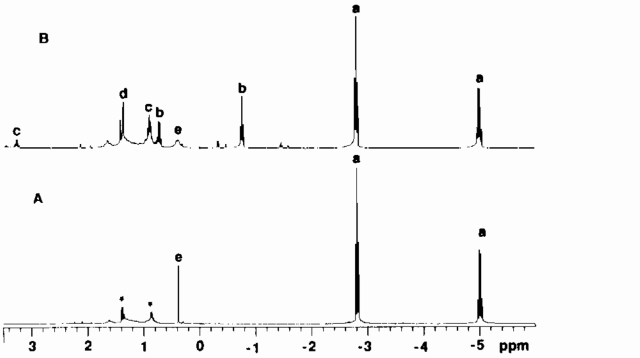


Fig. 4. ^1H NMR spectra of a benzene-d_6 solution of (TPP)$Ga(C_2H_5)$ under one atmosphere of dioxygen. A, without photolysis. B, after photolysis for 1.5 h. Peaks are labelled a for (TPP)$Ga^{III}(C_2H_5)$, b for (TPP)$Ga^{III}(OOC_2H_5)$, c for ethanol, d for acetaldehyde, e for water, and * for solvent impurities.

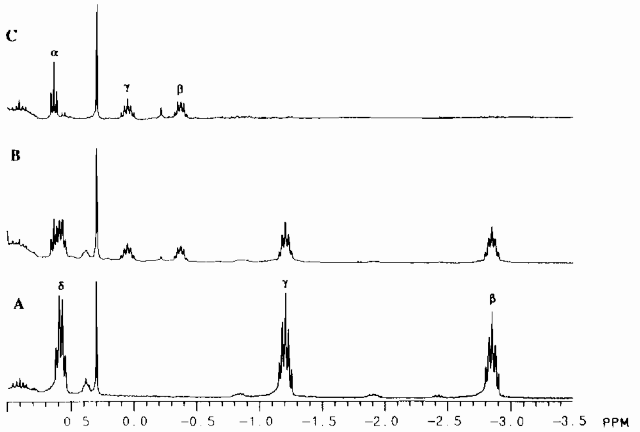


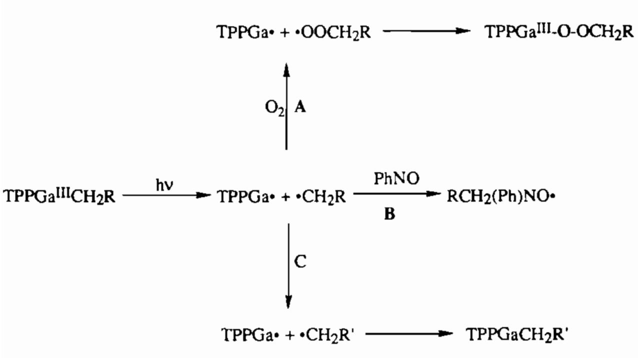
Fig. 5. ^1H NMR spectra of a benzene-d_6 solution of (TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$ (**2**) under one atmosphere of dioxygen: A, before photolysis; B, after 1.5 h of photolysis; C, after 3 h of photolysis. Resonances in trace A are labelled following the structure shown for **2**. In trace C α, β and γ refer to the protons of (TPP)$Ga^{III}(OOCH_2)(\alpha)CH_2(\beta)CH_2(\gamma)CH_2CH{=}CH_2$).

Figure 5 shows the effects of photolysis of a solution of (TPP)$Ga^{III}((CH_2)_4CH{=}CH_2)$ (**2**) in benzene-d_6 under one atmosphere of dioxygen at 23 °C. Trace A shows a portion of the ^1H NMR spectrum of **2** before photolysis. Trace B shows the spectrum after 1.5 h of photolysis while trace C shows the spectrum after 3 h of photolysis. During the photolysis the resonances of **2** decrease in intensity while a new set of axial ligand resonances appear at lower field. Notice that there is no evidence of isomerization of **2** to **1** under these conditions. The product observed in traces B and C can be confidently identified as (TPP)$Ga^{III}(OO(CH_2)_4CH{=}CH_2)$. The resonances are clearly distinct from those of (TPP)$Ga^{III}(O(CH_2)_4CH{=}CH_2)$

(Table 1) which has been prepared independently. The presence of a distinct triplet at 0.4 ppm is indicative of the presence of a α-$\mathrm{CH_2}$ unit that is adjacent to a methylene not a methine unit. The formation of $\mathrm{(TPP)Ga^{III}(OOCH_2CH(CH_2)_4)}$ would have produced a characteristic doublet in that region of the spectrum. Additionally the characteristic multiplets of all portions of the axial ligand have been observed as set out in Table 1.

Discussion

The results described above indicate that photolysis of $\mathrm{TPPGa^{III}CH_2R}$ results in homolytic cleavage of the Ga–C bond. Subsequent reaction of the alkyl radical can lead to a variety of products depending on conditions. These are summarized in Scheme 1. In the presence of dioxygen, the alkyl radicals are trapped to form alkylperoxo radicals (path A). These can recombine with the photolytically produced gallium radical to form the peroxy complex $\mathrm{TPPGa^{III}OOCH_2R}$. The formation of these peroxy complexes has been observed with either an ethyl or a 5-hexenyl group as the axial ligand. In the presence of nitrosobenzene, the alkyl radicals are trapped to form stable nitroxide radicals as shown by the ESR data in Fig. 3 (path B). In the absence of a trapping agent, photolysis of $\mathrm{TPPGa^{III}((CH_2)_4CHCH_2)}$ (**2**) results in its isomerization to form $\mathrm{TPPGa^{III}(CH_2CH(CH_2)_4)}$ (**1**). This can occur by homolysis followed by rearrangement (reaction 1) and recombination (path C). The lack of cyclization in the photolytic formation of $\mathrm{TPPGa^{III}}$-$\mathrm{(OOCH_4CH{=}CH_2)}$ simply results from the fact that reaction with dioxygen (path A) occurs faster than cyclization (path C). Once the peroxy radical forms it does not undergo cyclization.



Scheme 1.

Experimental

Preparation of compounds

$\mathrm{(TPP)Ga^{III}(OH)\cdot H_2O}$ [10], $\mathrm{(TPP)Ga^{III}C_2H_5}$ [8, 9], $\mathrm{(TPP)Ga^{III}Cl}$ [8] and ethyl hydroperoxide [19] were prepared by previously reported routes.

$\mathrm{(TPP)Ga^{III}(CH_2CH(CH_2)_4)}$ (1)

A solution of 4.5 equiv. of cyclopentamethyl magnesium bromide (from cyclopentamethylbromide and magnesium) in THF was added to a solution of 20 mg of $\mathrm{(TPP)Ga^{III}Cl}$ in 20 ml of toluene. The solution turned form dark pink to dark green almost immediately. After the solution was stirred for 15 min, 1 ml of dioxygen-free water was added. The mixture was dried over magnesium sulfate and then placed on a 10 mm × 20 mm column of basic alumina and eluted with toluene under dinitrogen atmosphere. The green band was collected and evaporated to dryness to produce the product as a purple solid. ^{1}H NMR (ppm) in $\mathrm{C_6D_6}$: porphyrin resonances: pyrrole, 9.10(s); *ortho*, 8.14 (s, broad); *meta* and *para*, 7.45(m); axial ligand resonances are in Table 1.

$\mathrm{(TPP)Ga^{III}((CH_2)_4CH{=}CH_2)}$ (2)

This was prepared using the procedure described for **1** with the Grignard reagent formed from 5-hexenyl bromide and magnesium in THF solution. Solutions of the product are green while the isolated solid is purple: UV–Vis λ_{max} (nm) (ϵ ($\mathrm{cm^{-1}\ M^{-1}}$)) in toluene: 442 (2.73×10^5), 536 (3.49×10^3), 576 (1.12×10^4), 618 (9.38×10^3). ^{1}H NMR (ppm) in $\mathrm{C_6D_6}$: porphyrin resonances: pyrrole, 9.10(s); *ortho*, 8.14 (s, broad); *meta* and *para*, 7.45(m); axial ligand resonances are in Table 1. The electron impact mass spectrum showed parent ions at 763 and 765 a.m.u. for ^{69}Ga and ^{71}Ga, respectively.

$\mathrm{(TPP)Ga^{III}(OC_2H_5)}$

A solution of n-butyl lithium (1 ml of a 1.6 M solution) was added to 1 ml (0.034 mol) of 100% ethanol (distilled from magnesium turnings) in 25 ml of diethyl ether at −78 °C. The solution was warmed to room temperature and stirred for 30 min. A 0.5 ml portion of this solution was added to 13 mg (0.018 mmol) of $\mathrm{(TPP)Ga^{III}Cl}$ in 15 ml of dried toluene (distilled from sodium metal). The mixture was stirred for 1 h. The dark pink solution was filtered to remove a white solid (lithium chloride) and evaporated to dryness to yield the product as a purple-pink solid. UV–Vis λ_{max} (nm) (ϵ ($\mathrm{cm^{-1}\ M^{-1}}$)): 422 (6.55×10^5), 514 (3.67×10^3), 552 (2.47×10^4), 590 (4.65×10^3). ^{1}H NMR (ppm) in $\mathrm{C_6D_6}$: porphyrin resonances: pyrrole, 9.09(s); *ortho*, 8.06(d); *meta* and *para*, 7.44(m); axial ligand resonances are in Table 1. The other alkoxide complexes were prepared similarly.

(TPP)Ga(OOt-Bu)

100 μl a 90% t-BuOOH solution (0.9 mmol) was added to 10 mg 0.014 mmol) of (TPP)GaOH·H_2O in 15 ml of a 98% benzene/2% methanol solution. Molecular sieves were added to absorb water and the mixture was stirred for 15 min. The pink solution was filtered gravimetrically and dried under vacuum to give a purple–pink solid. ^1H NMR (ppm) in C_6D_6; porphyrin resonances: pyrrole, 0.09(s), *ortho*, 8.05(d), *meta* and *para*, 7.45(m); axial ligand resonances are in Table 1. UV–Vis λ_{max}, (nm) (ϵ (cm^{-1} M^{-1})): 422 (4.67×10^5), 514 (2.12×10^3), 552 (1.62×10^4), 590 (3.15×10^3).

(TPP)Ga(OOC$_2$H$_5$)

A solution of 100 μL (1.5 mmol) of ethylhydroperoxide was added to 30 mg (0.042 mmol) of (TPP)Ga^{III}OH·H_2O in 25 ml of a 98% benzene/2% methanol solution. Molecular sieves were added to absorb water and the mixture was stirred for 15 min. The dark pink solution was filtered and evaporated to dryness to give the product as a purple solid. ^1H NMR (ppm): porphyrin resonances: pyrrole, 9.09(s); *ortho*, 8.06(d); *meta* and *para*, 7.45(m); axial ligand resonances are in Table 1.

Photolysis studies

A typical experiment involved the irradiation of a 3 mM solution of the complex in a 5 mm NMR tube by a 300 W tungsten source. The sample was contained in a condenser cooled by water during photolysis to prevent heat damage. For experiments under dioxygen, extra dry dioxygen (Matheson) was introduced into the sample via syringe for 2 min. For radical trapping experiments, a solution of nitrosobenzene in dioxygen-free C_6D_6 was added via syringe to the NMR tube.

Instrumentation

^1H NMR spectra were recorded at 300 MHz on a General Electric QE 300 spectrometer using a 4000 Hz spectral window, 32 K data points, a 1 s pre-pulse delay and a 3 μs pulse. 40 to 60 transients were acquired for each spectrum. ESR spectra were obtained at room temperature on a Varian E-4 EPR spectrometer.

X-ray crystallographic studies

Crystals of (TPP)Ga^{III}(CH(CH$_2$)$_4$)·$C_6H_5CH_3$ were obtained by diffusion of n-hexane into a toluene solution of the complex. A suitable crystal was mounted on a glass fiber with silicone grease and positioned in the cold stream of the X-ray diffractometer. Only random fluctuations (<2%) in the intensities of two standard reflections were observed during data collection. Crystal data are given in Table 4. The usual corrections for Lorentz and polarization effects were applied to the data. Crystallographic programs were those of SHELXTL PLUS. Scattering factors and corrections for anomalous dispersion were taken from a standard source [20].

TABLE 4. Crystallographic data for (TPP)Ga^{III}-(CH$_2$CH(CH$_2$)$_4$)·$C_6H_5CH_3$

Formula	$C_{57}H_{47}N_4Ga$
Formula weight	857.7
Space group, crystal form	$P\bar{1}$, triclinic
a (Å)	10.877(3)
b (Å)	11.389(2)
c (Å)	18.786(3)
α (°)	81.02(2)
β (°)	79.19(2)
γ (°)	74.36(2)
V (Å^3)	2187.5(8)
Z	2
T (K)	130
λ(Cu Kα) (Å)	1.54178
μ(Cu Kα) (mm^{-1})	1.160
D_{calc} (Mg m^{-3})	1.302
Transmission factors	0.50–0.83
$R(F_o)$	0.069
$R_w(F_o)$	0.071

The structure was solved using direct methods. The structure shows disorder in the gallium locations with site Ga with 90% occupancy and site Ga′ with 10% occupancy. An absorption correction was applied [21]. The method obtains an empirical absorption tensor from an expression relating F_o and F_c. Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were included at calculated positions by a riding model with a C–H distance of 0.96 Å and $U_H = 1.2U_C$.

Supplementary material

Tables of crystal data, bond lengths, bond angles, hydrogen atom positions and anisotropic thermal parameters and tables of observed and calculated structure factors are available from the authors.

Acknowledgement

We thank the National Institutes of Health (GM 26226) for financial support.

References

1 R. D. Arasasingham, A. L. Balch and L. Latos-Grażyński, *J. Am. Chem. Soc., 109* (1987) 5846.

2 R. P. Arasasingham, A. L. Balch, C. R. Cornman and L. Latos-Grażyński, *J. Am. Chem. Soc., 111* (1989) 4357.

3 A. L. Balch, R. L. Hart, L. Latos-Grażyński and T. G. Traylor, *J. Am. Chem. Soc., 112* (1990) 7382.

4 R. D. Arasasingham, C. R. Cornman and A. L. Balch, *J. Am. Chem. Soc., 111* (1989) 7800.

5 A. L. Balch, C. R. Cornman and M. M. Olmstead, *J. Am. Chem. Soc., 112* (1990) 2963.

6 C. Cloutour, D. La Farquer and J. C. Pommier, *J. Organomet. Chem., 190* (1980) 35.

7 D. Griller and K. U. Ingold, *Acc. Chem. Res., 13* (1980) 317; M. Julia, *Acc. Chem. Res., 4* (1971) 386.

8 A. Coutsolelos and R. Guilard, *J. Organomet. Chem., 253* (1983) 273.

9 K. M. Kadish, B. Boisselier-Cocolios, A. Coutsolelos, P. Mitaine and R. Guilard, *Inorg. Chem., 24* (1985) 4521.

10 K. M. Kadish, J.-L. Cornillon, A. Coutsolelos and R. Guilard, *Inorg. Chem., 26* (1987) 4157.

11 A. Boukhris, C. Lecomte, A. Coutsolelos and R. Guilard, *J. Organomet. Chem., 303* (1986) 151.

12 R. C. Lamb, P. W. Ayers, M. K. Toney and J. F. Gurst, *J. Am. Chem. Soc., 88* (1966) 4261.

13 H. W. J. Bodewitz, C. Blomberg and F. Bickelhaupt, *Tetrahedron, 31* (1975) 1053.

14 M. P. Byrn and C. E. Strouse, *J. Am. Chem. Soc., 113* (1991) 2501.

15 A. Coutsolelos, R. Guilard, A. Boukhris and C. Lecomte, *J. Chem. Soc., Dalton Trans.,* (1986) 1779.

16 A. Coutsolelos, R. Guilard, D. Baywell and C. Lecomte, *Polyhedron, 5* (1986) 1157.

17 K. M. Waggoner and P. P. Power, *J. Am. Chem. Soc., 113* (1991) 3385.

18 M. A. Petrie, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc., 113* (1991) 8704.

19 H. R. Williams and H. S. Mosher, *J. Am. Chem. Soc., 76* (1954) 2984.

20 *International Tables for X-ray Crystallography,* Vol. 4, Kynoch, Birmingham, UK, 1974.

21 B. Moezzi, *Ph.D. Thesis,* University of California, Davis, 1987.