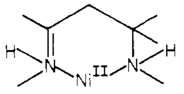

it is required that the hydrogen to be lost on the C–H group will be with the right configuration relative to the nitrogen. This is always the case for $\mathrm{Ni^{III}L_1}$, as there are two hydrogens on the carbon, and might not be the case for $\mathrm{Ni^{III}L_2}$ and $\mathrm{Ni^{III}L_3}$. This factor might also contribute to the differences observed in the stabilization caused by sulfate of the latter two complexes.

Acknowledgment. This work was supported in part by a grant from the United States–Israel Binational Foundation (BSF), Jerusalem, Israel. E.Z. appreciates a fellowship from the Casali Foundation.

Registry No. $\mathrm{NiL_2^{2+}}$, 47105-35-1; α-$\mathrm{NiL_3^{2+}}$, 51372-00-0; β-$\mathrm{NiL_3^{2+}}$, 51371-74-5; α-$\mathrm{NiL_3(SO_4)_2^-}$, 78821-58-6; β-$\mathrm{NiL_3(SO_4)_2^-}$, 78739-34-1.

Notes

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Novel Peroxo Complexes of Uranium Containing Organic Ligands

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Peroxo complexes of molybdenum and tungsten are attracting interest as oxidants in organic synthesis.[1-5] As uranium somewhat resembles the group 6B elements, it was of interest to discover whether it would form analogous peroxo complexes which contain organic moieties. The preeminence of the UO_2 grouping distinguishes uranium from molybdenum and tungsten, however, and this factor may have hitherto prevented the generation of peroxo complexes from uranyl salts and organic reagents. The present paper describes the isolation and characterization of novel mono- and diperoxo complexes. These are found to be unusually stable, and they are relatively unreactive. they are the first reported examples of peroxo complexes of uranium which contain organic moieties.

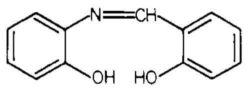
Experimental Section

The organic reagents (Eastman) were used as supplied.

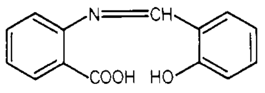
Purification of Solvents. Spectrograde acetone was dried by cooling in the presence of NaI to form crystals of $(CH_3)_2CONaI$. The acetone was recovered by warming to 30 °C and then distilling. Other solvents were simply distilled.

Preparation of UCl_4. The compound formed when CCl_4 vapor entrained in a stream of dry N_2 was passed over U_3O_8 in a tube held at 500 °C for 2.5 h.

Preparation of Schiff Bases. *N*-(2-Hydroxyphenyl)salicylidenimine is identified hereafter as L. A solution of 2-aminophenol (0.1 mol, 10.9 g) in a 1:1 mixture of benzene and ethanol (100 mL) was added to a solution of salicylaldehyde (0.1 mol, 12.2 g) in benzene (20 mL). The resulting mixture was boiled for 3 min and then cooled in an ice–salt bath whereupon bright reddish yellow crystals formed. these were separated, washed several times with hot ethanol, and dried in vacuo over magnesium perchlorate; yield 16.1 g. Recrystallization was from methanol. Anal. Calcd for $C_{13}H_{11}NO_2$: C, 73.23; H, 5.16. Found: C, 73.22; H, 5.16.



L



L′

N-(2-Carboxyphenyl)salicylidenimine is identified hereafter as L′. This was obtained when a solution of 2-aminobenzoic acid (0.1 mol, 13.7 g) in a 1:1 mixture of benzene and ethanol (100 mL) was added to a solution of salicylaldehyde (0.1 mol, 12.2 g) in benzene (20 mL). The resulting solution was heated on a steam bath for 5 min and then cooled in an ice–salt bath. Yellow crystals were separated and washed with benzene and ethanol; yield 17.0 g. Recrystallization was from methanol. Anal. Calcd for $C_{14}H_{11}NO_3$: C, 69.70; H, 4.56. Found: C, 69.7; H, 4.55.

Preparation of Complexes. The complexes and their elemental analyses are listed in Table I. Complexes of U(IV) were prepared by addition of a stoichiometric quantity of the ligand to UCl_4 in acetone. Two different approaches were used to synthesize peroxo complexes. Peroxo complexes containing multidentate ligands were prepared by adding H_2O_2 (50%) to solutions of the U(IV) intermediates in methanol (compound **13**) or a 1:1 mixture of acetone and methanol (compounds **14–17**). When U(IV) adducts of the unidentate ligands were dissolved in boiling acetone or methanol prior to the addition of H_2O_2, the product was $UO_4{\cdot}4H_2O$. However, complexes containing monodentate ligands were successfully converted to peroxo complexes of U(VI) by moistening the crystals in succession with acetone and H_2O_2 (50%) and warming.

Analyses. Uranium was determined gravimetrically.[8] Methanolic solutions of the peroxo complexes were titrated with Ce(IV) to determine the number of active oxygen atoms present.[9] The titrations (Table II) indicated that complexes **10–12** and **13–17** are di- and monoperoxo complexes, respectively.

Infrared spectra (Nujol mulls) were recorded with a Pye Unicam SP1100 or a Beckman IR-20 spectrophotometer. Spectra between 1500 and 200 cm^{-1} for some complexes were obtained with a Perkin-Elmer 283 spectrophotometer. Raman spectra of the solids were obtained with a Spectra-Physics Model 125A He–Ne laser operated at 50–60 mW. The 6328-Å line was used, and the spectra were calibrated by means of the neon lines. Proton and ^{13}C NMR spectra were obtained with Varian T-60 and FT-80 spectrophotometers. Tetramethylsilane was employed as internal standard.

Results and Discussion

Complexes of Uranium(IV). Several complexes which served as precursors of the peroxo compounds are described below. Compounds **2** and **3** have been reported previously.[6,7] The U(IV) complexes were soluble in almost all of the polar solvents tried, and the electrical conductivities of 5×10^{-4} M solutions in nitromethane or nitrobenzene indicated that all of the complexes were undissociated.

Infrared data are shown in Table III. Complex **1** shows a decrease in ν(N–O) compared to the value for free pyridine

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Table I. Analytical Data and Other Physical Properties of the U(IV) and U(VI) Complexes

		% U		% C		% H			
no.	compd	calcd	found	calcd	found	calcd	found	color	mp,[a] °C
1	$[UCl_4 \cdot 2ONC_5H_5]$	41.90	41.85	21.12	21.11	1.76	1.73	green	270
2	$[UCl_4 \cdot 2OPPh_3]$	25.48	25.37					pale green	319-322
3	$[UCl_4 \cdot 2OAsPh_3]$	23.28	23.26	42.27	42.15	2.94	3.0	pale green	310-311
4	$[U(C_5H_3N(COO)_2)_2]$	41.90	41.78	29.57	29.41	1.05	1.04	green	345-347
5	$[U(C_6H_4NH_2O)_2(H_2O)Cl_2]$	43.91	43.86	26.56	26.39	2.58	2.51	green	330-331
6	$[U(C_5H_4NCOO)_2Cl_2] \cdot C_5H_4NCOOH$	35.25	35.01	32.0	31.65	1.92	1.95	pale green	275
7	$[U(C_6H_4NH_2COO)_2Cl_2] \cdot C_6H_4NH_2COOH$	33.19	33.3	35.14	34.78	2.37	2.43	green	280
8	$[U(C_{13}H_9NO_2)_2]$	36.06	36.25	47.27	46.79	2.72	2.62	greenish brown	291-293
9	$[U(C_{14}H_9NO_3)_2]$	33.24	33.07	46.92	46.85	2.51	2.63	brownish green	319-322
10	$[U(O)(O_2)_2 \cdot 2ONC_5H_5] \cdot H_2O$	45.24	45.21	22.81	22.64	2.28	2.29	yellow	335-338
11	$[U(O)(O_2)_2 \cdot 2OPPh_3] \cdot H_2O$	26.68	26.61	48.43	48.65	3.58	3.57	yellow	>360
12	$[U(O)(O_2)_2 \cdot 2OAsPh_3] \cdot H_2O$	24.28	24.40	44.08	43.69	3.26	3.13	pale yellow	>360
13	$[U(O)(O_2)(C_5H_3N(COO)_2)(H_2O)]$	50.74	50.90	17.91	18.30	1.06	1.05	yellow	351-353
14	$H^+[U(O)_2(O_2)C_6H_4NH_2O)(H_2O)]^-$	55.47	55.25					deep yellow	b
15	$H^+[U(O)_2(O_2)(C_5H_4NCOO)(H_2O)^-$	53.72	53.88	18.96	18.67	1.58	1.60	yellow	>360
16	$H^+[U(O)_2(O_2)(C_6H_4NH_2COO)(H_2O)]^-$	52.07	52.32	18.38	18.62	1.96	2.01	pale yellow	>360
17	$[U(O)(O_2)(C_{14}H_9NO_3)(H_2O)]$	43.83	43.72	30.93	31.25	2.02	2.03	deep yellow	336-340

[a] Uncorrected. [b] The complex decomposes at room temperature on standing.

Table II. Titration of Methanolic Solutions of the Peroxo Complexes by Aqueous Acidified Standard Ceric Sulfate Solution

complex no.	N[a]	complex no.	N[a]
10	4.2	14	2.05
11	4.1	15	1.95
12	3.95	16	2.08
13	2.2	17	1.75

[a] Number of equivalents of ceric sulfate per mole of complex.

oxide (1242 cm^{-1})[10] which is attributed to a decrease in the N–O bond order as a result of coordination to the metal atom. Complex **4** exhibits a strong carboxylato band at 1675 cm^{-1}. This is significantly shifted with respect to the uncoordinated pyridine-2,6-dicarboxylic acid (1710 cm^{-1}). This ligand is probably tridentate, the coordination sites being the nitrogen atom and the two carboxylato groups. The very strong band of compound **4** at 268 cm^{-1} can be tentatively attributed to the ν(U–N) mode.[11] So that additional evidence that the ligand nitrogen is bonded to uranium could be gained, an attempt was made to obtain a ^{13}C NMR spectrum of compound **4**. Dimethyl sulfoxide was the only effective solvent but the solutions rapidly formed a green precipitate which was presumably an adduct of Me_2SO. The infrared spectrum of the precipitate displayed a very strong band at 960 cm^{-1} characteristic of ν(S–O) in adducts of Me_2SO.[12] Jacobson et al.[13] found by X-ray structure determination and spectroscopic measurements that the nitrogen atom of the pyridinedicarboxylato ligand is coordinated to the metal atom in a number of compounds of Mo and W. Similarly, for complex **4**, elemental analysis, conductivity, and infrared data indicate a six-coordinate complex in which two coordination sites are occupied by nitrogen atoms.

Complexes **5** and **7** show two medium intensity bands (**5**, 3365 and 3290; **7**, 3230 and 3130 cm^{-1}—significantly lower than the values for 2-aminophenol and 2-aminobenzoic acid (3414, 3342 and 3390, 3300 cm^{-1})) which indicate coordination by nitrogen. Complexes **6** and **7** show very strong carboxylato bands at 1675 and 1615 cm^{-1}, respectively. However, these complexes also show bands at 1725 and 1680 cm^{-1} as expected for the free carbonyl group in pyridine-2-carboxylic acid and aminobenzoic acid, respectively. In addition, two weak bands appear at 3390 and 3300 cm^{-1} in complex **7**, characteristic of the uncoordinated amino group. Jacobson et al.[13] reported some compounds of Mo and W containing uncoordinated ligand molecules in the solid state. So that additional information on coordination of the picolinato ligand in complex **6** could be obtained, a ^{13}C NMR spectrum in dimethyl-d_6 sulfoxide was obtained. The spectrum was weak, but it appeared to show two types of carboxylic carbons with chemical shifts of 167.2 and 166.0 (166.3) ppm (the values in parentheses refer to free pyridine-2-carboxylic acid in dimethyl-d_6 sulfoxide). The signals assigned to carbon in positions 6 and 2 appeared at 144.9 (149.3) and 143.4 (148.3) ppm, respectively, whereas the signal of the carbon in position 4 was shifted downfield to 139.0 (137.8) ppm. The spectrum showed a broad band at 129–130 ppm which presumably arises from carbon 3 (124.8 ppm) and carbon 5 (127.2 ppm). However, we observed only one set of ring carbons. Presumably, one picolinic acid molecule utilizes its ring nitrogen to form a seven-coordinate uranium species in solution although apparently not in the crystal. The directions of the changes are analogous to those observed on protonation of pyridine.[14] Jacobson et al.[13] also reported similar changes in the Mo and W complexes of picolinic acid. Alkalimetric titrations of **6** and **7** dissolved in methanol exhibited inflection points at pH 3.6 and 3.8, respectively, at a stoichiometry of ca. 1.1 mol of NaOH per mole of complex. This is attributed to the neutralization of the free carboxylic acid protons.

The Schiff bases behaved as tridentate dinegative ligands coordinating at the imino nitrogen and two oxygen atoms. The assignments shown in Table III are based on comparisons with related compounds.[15-17] In complexes **8** and **9**, the decrease in ν(C=N) by 35 and 25 cm^{-1}, respectively, relative to the free ligands indicates that bond formation takes place through the imino nitrogen atom.[18] The ν(O–H) band observed in the free Schiff bases disappears upon coordination which indicates deprotonation and coordination at the oxygen site. Furthermore, in complex **9**, the coordination of the carboxylato group is evident from the negative shifting of ν(C=O) by 25

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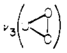
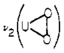
Table III. Infrared and Raman Spectral Data for the U(IV) and U(VI) Complexes[a]

compd no.	band maxima, cm^{-1}									
	ν(O–H)	ν(N–H)	ν(C=O)	ν(U=O)	ν(C=N)	ν(E=O)	ν_1(O–O)	ν_3 	ν_2 	other bands
1						1215 vs				ν(U–Cl) 250 vs
2						1060 vs				250 vs
3						845 vs				264 vs
4			1675							(ν(U–N)) 268
5	3500	3365 m, 3290 m								
6			1725 vs, 1675 vs							
7		3230 m, 3130 m, 3390 br, 3300 w	1680 vs, 1615 vs							
L	3290 br				1640 ms					
L′	3120 ms		1700 br		1625 ms					
8					1605 ms					
9			1675 br		1600 ms					
10	3525 br			915 vs		1209 vs	820 s	630 w	600 m	485 s, 200 s, 250 w
11	3500 br			922 vs		1070 vs	830 s	685 ms	606 ms	410 m, 250 m, 200 w
12	3500 br			907 vs		847 vs	805 s	670 ms	612 m	400 br, 240 s, 342 s
13	3500 br		1680 vs, 1660 vs	940 vs			860 vs, 825 s	661 w	588 w	415 br, 140 vs
15	3400 br		1650 s	930 vs			803 s	670 ms	610 w	490 w, 395 br, 238 s
16	3400 br	3200 m, 3105 m	1600 s	920 vs			825 ms	680 w	600 w	420 br, 240 s
17	3330 br		1634 br	915 vs	1590		805 s	670 ms	610 w	460 br, 240 m, 185 br

[a] Relative band intensities are denoted by vs, ms, s, m, w, br, meaning very strong, medium strong, strong, medium, weak, and broad, respectively. E stands for As, N, and P.

cm^{-1} from the free ligand value. The solid-state reflectance spectra of some complexes of U(IV) exhibited bands at 18 × 10^3 and 29 × 10^3 cm^{-1}. The former is due to a transition from the ground state A_1 ($^3H_4$) to higher levels within the $5f^2$ configuration[7] and the latter is caused by charge transfer.

Complexes of Uranium(VI). The peroxo complexes are formulated in Table I as seven-coordinate by analogy to similar complexes of Mo and W. It is conceivable that compounds **10–12** are actually eight-coordinate with the water molecule contained in the coordination sphere. All of the peroxo complexes display a very strong band at 907–940 cm^{-1} (Table III) corresponding to the ν(U=O) stretch.[10,19] Compounds **10–12** exhibit single bands at 485, 410, and 400 cm^{-1} assigned to U–O′ stretching (O′ = oxygen in organic ligand). The absence of band splitting possibly indicates a trans arrangement of the ligands although coupling of independent oscillators may be damped by the heavy metal atom.[20] In complex **11**, complexing causes a decrease in ν(P–O) by 122 cm^{-1} compared to the free ligand value.[21] In complex **12** the ν(As–O) is decreased by 33 cm^{-1} from the free ligand value.[22]

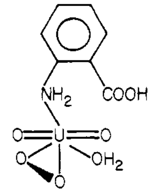
The metal peroxo grouping (local C_{2v} symmetry) gives rise to three infrared- and Raman-active vibrational modes. These are predominantly O–O stretching (ν_1), the symmetric M–O stretch (ν_2), and the antisymmetric M–O stretch (ν_3). Wendling[23] and Griffith[24] have clearly established that the ν_1 mode in compounds of Mo and W appears at 800–900 cm^{-1}, and bands at 500–650 cm^{-1} are likely to arise from ν_2 and ν_3 modes. There is however, a decrease in ν_1 upon passing from a molybdenum complex to the corresponding tungsten complex.[3,23,24] The present work extends the above trend to uranium where there is a further decrease in ν_1 to 803–860 cm^{-1}. In the present examples, ν_2 and ν_3 modes appear at 588–612 and 661–685 cm^{-1}, respectively, i.e., somewhat higher than in the Mo and W complexes. The Raman spectrum for **13** shows two well-defined bands in the O–O stretching region which presumably arise from two of several possible isomers.

Westland et al.[3] have reported that the O–O stretching frequency in peroxo complexes of Mo and W is descreased by replacing a given ligand by one which is a stronger donor. They argued that Ph_3AsO is more polar than Ph_3PO and is hence a stronger donor. This argument seems to apply again in accounting for the lower ν_1 value observed for **12** as compared to **11**.

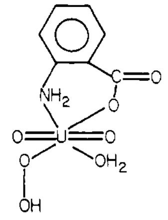
It is noteworthy that the ν_1 mode of the peroxouranium group is observed only in the Raman spectrum. the group appears to be behaving as if it has essentially linear symmetry, i.e., it is ionic. The same is observed with thorium complexes.[25]

The solid-state reflectance spectra of U(VI) peroxo complexes exhibited only a charge-transfer band at 29 × 10^3 cm^{-1}.

The complexes **14–16** are anionic. The formulations shown in Table I follow from the elemental analyses, conductivity measurements, and titrations with base and ceric ion (Table II). Alkalimetric titrations indicated an inflection point at pH 3.4–6.8 which corresponds to the neutralization of the outer-sphere proton. The molar conductivities of 5 × 10^{-4} molar solutions were about 10 Ω^{-1} cm^2 at 25 °C in both nitromethane and methanol, i.e., they are weak electrolytes. It is proposed that the low conductivities result from the formation in organic media of structures like **16a** and **16b**. Analogous conclusions were reached by Jacobson et al.[13] for analogous compounds of Mo and W.



16a



16b

So that the possible reactivity of the uranium peroxo complexes toward olefins could be explored, the complexes, typ-

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ically 0.6 mmol, were suspended in mesitylene and the stoichiometric quantity of cyclohexene or cyclooectene was added. Refluxing for 36 h failed to produce a reacion. Negative results were also found by Olah and Welch for Na_2UO_8.[26] However, refluxing of compound **15** (0.002 mol.) in allylalcohol for 20 h at 80 °C and subsequent cooling in dry ice–CCl_4 for 1 h produced the allylalcohol epoxide as monitored by TLC. This conclusion is supported by the proton NMR spectrum of the reaction product which shows narrow multiplets centered at 2.7, 3.1, and 3.6 ppm as required for allylalcohol epoxide.

Registry No. **1**, 78435-89-9; **2**, 16923-61-8; **3**, 24564-38-3; **4**, 64121-21-7; **5**, 78456-39-0; **6**, 78435-90-2; **7**, 78435-91-3; **8**, 78435-92-4; **9**, 78435-93-5; **10**, 78456-40-3; **11**, 78435-94-6; **12**, 78435-95-7; **13**, 78435-96-8; **14**, 78435-97-9; **15**, 78435-98-0; **16**, 78435-99-1; **17**, 78436-00-7; L, 1761-56-4; L′, 7361-93-5; 2-aminophenol, 95-55-6; salicylaldehyde, 90-02-8; 2-aminobenzoic acid, 118-92-3.

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Photochemistry of (Dioxygen)bis(triphenylphosphine)palladium in Chlorinated Hydrocarbon Solvents

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Received January 8, 1981

The photochemical reactivity of charge-transfer excited states has been a subject of increasing interest.[1-4] In order to probe the properties of metal to ligand charge-transfer excited states, we began an investigation of zerovalent, d^{10} palladium complexes with ligands having low optical negativity of the type PdL_4 (L = Ph_3, PPh_2Me) and PdL_2 (L = diphos). Because of the full d shell, the lowest energy electronic transitions involving the metal 4d orbitals are metal to ligand charge transfer. These complexes possess the additional properties of being simple to prepare and handle and of having a rich and well-characterized thermal chemistry.[5-8]

Early in the course of our investigations, we found that the compounds were highly photoactive in halogenated hydrocarbon solvents but did not give strictly reproducible results. Further investigation revealed that the photochemistry was very sensitive to the presence of trace amounts of oxygen and that the majority of reactions we observed originated from PdL_2O_2. In this note we report the photochemistry of PdL_2O_2 in dichloromethane solution.

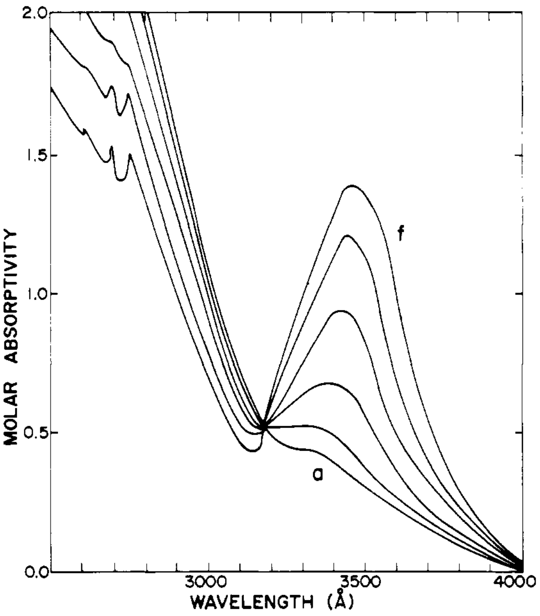


Figure 1. Spectral changes during irradiation of a 1.76×10^{-4} M solution of $Pd(PPh_3)_2O_2$ in dichloromethane: (a) no irradiation; (b) irradiation time of 15 s; (c) 30 s; (d) 60 s; (e) 90 s; (f) 120 s.

Experimental Section

Compounds. $Pd(PPh_3)_4$ was prepared from $PdCl_2$ and PPh_3[9] with use of the literature method.[9] $Pd(diphos)_2$ and $Pd(PPh_2Me)_4$ were prepared by adapting the same method with the use of appropriate ligands. The PdL_2O_2 complexes were prepared by the method of Wilkinson[7] while PdL_2Cl_2 was prepared by the method of Tayim.[8] All solvents were distilled at least twice before use and in some instances were degassed by blowing N_2 through the solvent followed by freeze–pump–thaw cycles.

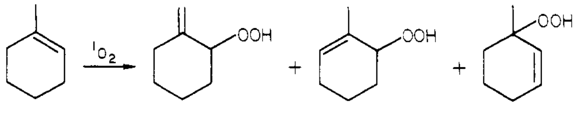
Instrumentation. The electronic absorption spectra and the absorbance changes for the quantum yield measurements were taken with a Cary 14 spectrometer and a Hitachi PE 139 UV–visible spectrometer, respectively. Infrared absorption spectra were taken with a PE 521 grating IR spectrophotometer.

Photolysis was carried out with use of a Hanovia 1000-W high-pressure mercury–xenon lamp or a 100-W mercury lamp. The light from the 1000-W lamp was collimated and filtered to provide a parallel 405-nm beam. A transmission spectrum of the filtered light revealed that the 405-nm line was contaminated with a small amount of the 438-nm line. The 100-W lamp was selectively filtered with use of a 7-51 Corning filter and a $CuSO_4$ solution to provide 366-nm light.

Photochemistry. All photochemical reactions were studied with use of an optical bench to ensure constant geometry. The radiation was incident on a 1-cm Cary cell (3-mL capacity) which was encased in water-cooling system to limit heating effects. The solutions were stirred by a magnetic stir bar to ensure uniform illumination. The photon flux from the filtered lamp was measured with use of ferrioxalate actinometry.[10]

The quantum yield of product formation was obtained in two ways. The appearance of an intense absorption peak at 345 nm corresponding to PdL_2Cl_2 was monitored at intervals during the photolysis and the quantum yield then calculated. In addition, the PdL_2Cl_2 production was also monitored by collecting and weighing the photoproduct. Disappearance of the Pd complex was followed by monitoring an IR band on the PE 521.

Singlet O_2 analysis was performed with 1-methylcyclohexene as a detector trap.[11] In the presence of singlet O_2, 1-methylcyclohexene reacts to form three peroxo compounds:



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