Aerobic Photooxidation and C–C Bond Cleavage of the Acetylacetonate Ligand in (2-Arylazo)arylpalladium(II) Complexes Induced by Visible Light

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(Arylazo)aryl(acetylacetonato)palladium(II) complexes, [Pd(4-$RC_6H_3N{=}NC_6H_4R$-4')(*O,O*-acac)] (R = H **1a**, Me **1b** or OMe **1c**; Hacac = acetylacetone), upon irradiation of their acetone solutions at room temperature by UV, or even long-wavelength visible ($\lambda > 500$ nm) light, were readily oxidized by atmospheric oxygen to give the corresponding acetato derivatives [Pd(4-$RC_6H_3N{=}NC_6H_4R$-4')(μ-O_2CMe)]$_2$ (R = H **2a**, Me **2b** or OMe **2c**), providing a model for some chemical and biological processes. The oxidation reaction of complex **1b** was first order in the complex when $[\mathbf{1b}]_0 \leqslant 2 \times 10^{-3}$ mol dm^{-3}. Complexes **1b** and **1c** were photooxidized at approximately twice the rate of complex **1a**. In the presence of a scavenger of C-centred radicals (CCl_4) the rate of complex **2b** accumulation was reduced. When pyridine was added or co-ordinating solvents (acetonitrile or nitromethane) were used no photooxidation of complex **1** occurred. In the presence of PPh_3 an induction period was observed and the oxidation of **1** started only after all the PPh_3 was oxidized under irradiation into $OPPh_3$. Spectroscopic data suggested that these ligands inhibit this photochemical oxidation because they change the type of co-ordination of the azobenzene chromophore and/or the acac ligands inducing a disconnection between the chromophore (antenna) and the acac ligand.

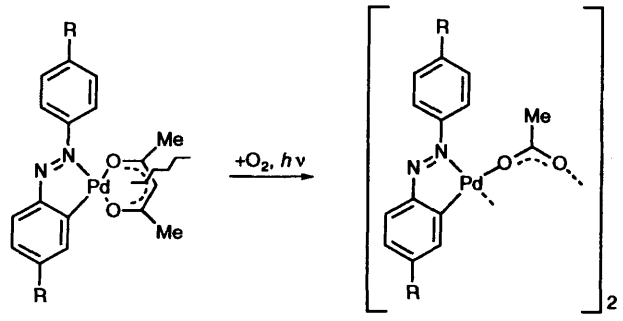
Reactions of organic compounds photosensitized by some organic acceptors (anthraquinone, dicyanoanthracene, *etc.*), dyes or pigments (porphyrins as well as metalloporphyrins and many others) and various metal complexes (*e.g.* polypyridyl derivatives) are of considerable interest because they are convenient synthetic methods,[1] they may be used as models of photosynthesis in the design of systems that are capable of converting sunlight into stored chemical energy[2] and are applied in photoimaging systems.[3] Among these reactions, the photooxidation with molecular oxygen (autooxidation) attracts great attention from both chemists and biologists. Indeed, photochemical autooxidation gives valuable products (ketones, acids, peroxides, *etc.*).[4] Often, such a process includes an electron-transfer stage.[5] In many cases, transient peroxides are formed that decompose to give the final C–C bond-cleavage products.[6] For example, photooxygenation of styrene or ethylbenzene, in the presence of cyclopentadienyl or bromide complexes of iron as catalysts, produces benzaldehyde.[7] On the other hand, photosensitized oxidation processes are known to occur in tissues stimulating their damage. Thus, for example, lipids may be peroxidized with subsequent C–C bond splitting,[8] and the oxidative interaction of DNA with ruthenium polypyridyl complexes promotes nucleic acid cleavage.[9] So called photodynamic therapy is based on the sensitized oxidation of biological matter in the target tissue[10] and is effective for the treatment of tumours,[11] *e.g.* cancer.[12]

Usually, photochemical autooxidation processes that proceed *via* an electron-transfer stage, and include the formation of radicals, demand illumination with short-wavelength (predominantly UV) light. A tempting task of contemporary photochemistry is to extend the sensitivity of such systems into the region of long-wavelength ($\lambda > 400$–500 nm) visible irradiation. Green plants and other light-harvesting organisms are known to use low-energy irradiation for photosynthesis.[2,13] These natural photosynthetic systems consist of antennae that absorb long-wavelength light energy and transfer it to reaction centres which use this energy to stimulate the chemical transformations. An analogous approach may be used not only for modelling some natural light-harvesting organisms but also for the design of systems that are capable of using low-energy irradiation to undertake various chemical reactions. Earlier, Whitten *et al.*[14] and Kutal and co-workers[15] described sensitization that involved the intramolecular transfer of energy from an unreactive chromophore of a metal complex to a reactive substrate bound to the metal. The reaction investigated was the *cis–trans* isomerization of 4-styrylpyridine co-ordinated to a chromophore fragment. Well known chromophore fragments, *i.e.* metalloporphyrins and cyclopalladated azobenzene,[16] were employed.

Here, we describe a system that uses absorbed long-wavelength light energy for autooxidation of an organic substrate and combines within one metal complex molecule, (*i*) the light-harvesting chromophore fragment (analogous in some aspects to an antenna in natural and artificial photosynthetic systems),[2,13] (*ii*) the (palladium ion) reaction centre, and (*iii*) the substrate for autooxidation, *i.e.* the acetylacetonate ligand. Some of these results have been the subject of a preliminary communication.[17]

Results and Discussion

We have found that (arylazo)aryl(acetylacetonato)palladium(II) complexes, [Pd(4-$RC_6H_3N{=}NC_6H_4R$-4')(*O,O*-acac)] (R = H **1a**, Me **1b** or OMe **1c**; Hacac = acetylacetone), are light-sensitive compounds which are readily oxidized by atmospheric oxygen when their solutions in acetone are illuminated. Corresponding acetato derivatives, [Pd(4-$RC_6H_3N{=}NC_6H_4R$-4')(μ-O_2CMe)]$_2$ (R = H **2a**, Me **2b** or OMe **2c**), are formed as main products. The reaction was followed in time by electronic spectroscopy. Fig. 1(*a*) illustrates the spectral changes that result upon irradiation of an acetone solution of complex **1b** with polychromatic light from a medium-pressure mercury arc in a Pyrex vessel ($\lambda > 300$ nm). During the first 10 min of irradiation, the transformation **1b** ⟶ **2b** occurs and an



1a R = H
1b R = Me
1c R = OMe

2a R = H
2b R = Me
2c R = OMe

isosbestic point at *ca.* 500 nm can be observed. Some minor differences in the spectra of the reaction solution and an authentic solution of complex **2b** [Fig. 1(*b*)] may be due to the concurrent formation of other complexes in smaller concentrations. Indeed, a few new weak spots besides the spot of **2b** can be detected by TLC. On prolonged irradiation of a solution of complex **1b**, a new absorption maximum appears at *ca.* 520 nm with concomitant reduction of the maximum at *ca.* 460 nm. Exactly the same changes were observed in the spectrum of an irradiated acetone solution of complex **2b** [Fig. 1(*b*)]. According to TLC (silica gel), at least four new products were formed from **2b**. These products were isolated by preparative TLC, but in too small amounts to be fully characterized. Thus, complexes **2** are also photosensitive and under irradiation slowly and unselectively transform into a set of products.

The kinetic curve of complex **2b** accumulation in time is shown in Fig. 2 (upper curve). If the solvent is distilled in a nitrogen atmosphere before irradiation, the rate of **2b** formation is much lower. In this case the yield of **2b** is also lower (Fig. 2, lower curve). The reaction appeared to occur until the traces of oxygen were removed from the reaction mixture by the oxidation process. Indeed, if a pulse of air is bubbled through the solution **2b** formation starts again. Thus, it may be concluded that complexes **2** are formed when complexes **1** are photochemically oxidized by atmospheric oxygen.

From the plot of the initial rates of the oxidation of complex **1b** (determined as concentrations of complex **2b** at the beginning of the irradiation) *versus* the initial concentrations of **1b** (Fig. 3) we may deduce that when $[\mathbf{1b}]_0 \leqslant 2 \times 10^{-3}$ mol dm^{-3} the oxidation reaction is first order in **1b**.

We investigated various sources of polychromatic light, not only UV but also visible and especially long-wavelength ($\lambda >$ 500 nm) irradiation. Naturally, the longer the wavelength of light used, the lower the rate of oxidation. The reaction **1b** ⟶ **2b** ($[\mathbf{1b}]_0 = 3 \times 10^{-4}$ mol dm^{-3}), followed in time by electronic spectroscopy, gave *ca.* 95% yield of the product after 10 min if a mercury arc ($\lambda >$ 300 nm) was used [Fig. 1(*a*) and Fig. 2 (upper curve)] and after 60 min if a 200 W standard tungsten lamp ($\lambda >$ 400 nm) was used (relative initial rates of complex **2b** accumulation, 1.0 and 0.1). When more concentrated (2×10^{-2} mol dm^{-3}) solutions of complex **1b** in acetone were exposed to sunlight ($\lambda >$ 270 nm) in a Pyrex flask for three weeks, dark red crystals of complex **2b** precipitated (54% yield). The photochemical transformation of **1a** was carried out also on the preparative scale. Thus, irradiation in air of a solution of **1a** (0.5 mmol) in acetone (20 cm^3) by the full light of a mercury arc for 14 h gave **2a** (66%), besides metallic palladium and minor amounts of other complexes and organic products (control by TLC; azobenzene and acetylated azobenzene were detected in the mixture by mass spectrometry). Complex **2a** was separated by column chromatography (silica gel, acetone eluent).

Irradiation, by an 'Osram Ultra Vitalux' lamp ($\lambda >$ 300 nm), of aerated solutions of complexes **1** in other non-co-ordinating solvents, *e.g.* methylene chloride or toluene, also leads to the

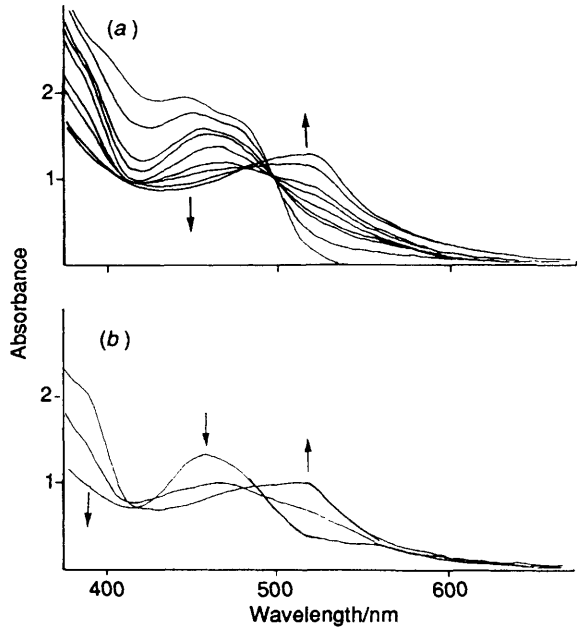


Fig. 1 Changes in the spectrum of an aerated acetone solution of (*a*) complex **1b** (3×10^{-4} mol dm^{-3}) during irradiation by full light from a medium-pressure mercury arc in a Pyrex vessel (curves after 0, 2, 5, 10, 30, 90, 150, 300 and 450 min of irradiation) and (*b*) complex **2b** (3×10^{-4} mol dm^{-3}) (curves after 0, 180 and 240 min of irradiation)

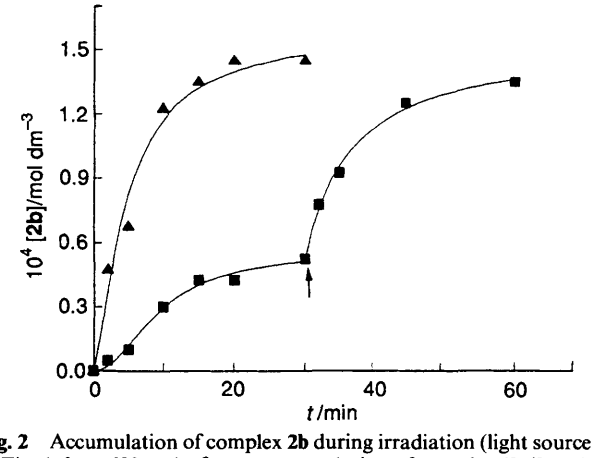


Fig. 2 Accumulation of complex **2b** during irradiation (light source as in Fig. 1, λ = 600 nm) of an acetone solution of complex **1b** (3×10^{-4} mol dm^{-3}) in air (▲) or in a N_2 atmosphere in acetone distilled under N_2 before irradiation (■). The arrow indicates when a pulse of air was bubbled through the solution

formation of complexes **2**, although reactions proceed with lower rates (0.6 and 0.2 respectively, relative to 1.0 for that in acetone). No oxidation, however, was observed when diluted solutions in co-ordinating solvents (*e.g.* acetonitrile or nitromethane) were used or pyridine or triphenylphosphine were added to acetone solutions. We assume that these solvents and other molecules (ligands L), which are capable of being co-ordinated to the palladium ion, form new photochemically inactive complexes **3** (see Scheme 1). It is interesting that in the case of L = PPh_3 the oxidation **1** ⟶ **2** proceeds, but only after an induction period. The higher the concentration of PPh_3 the longer the induction period (Fig. 4). In blank experiments, we have found that under irradiation triphenylphosphine, even in the absence of complex **1**, is rapidly oxidized with oxygen dissolved in acetone to produce phosphine oxide. So it is reasonable to propose that during the induction period in the transformation **1** ⟶ **2**, the PPh_3 unco-ordinated to palladium is photochemically oxygenated to $OPPh_3$ and, once all consumed, the inactive complex **3** reverts to the starting

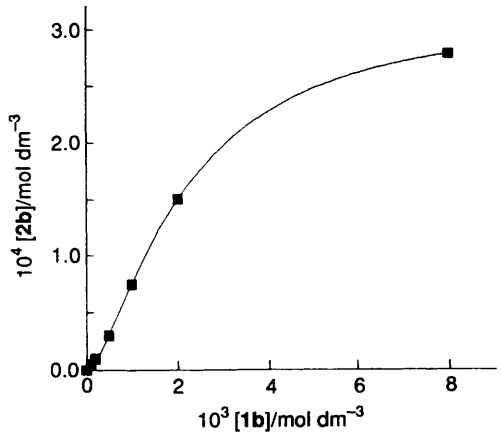


Fig. 3 Plot of concentration of complex **2b** after 2 min irradiation (light source as in Fig. 1) *versus* initial concentration of complex **1b**, dried acetone solutions

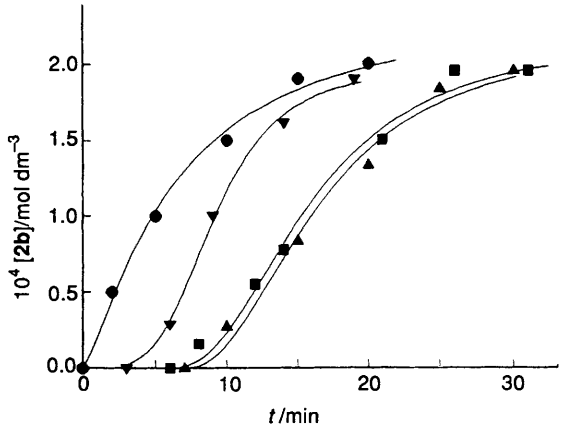
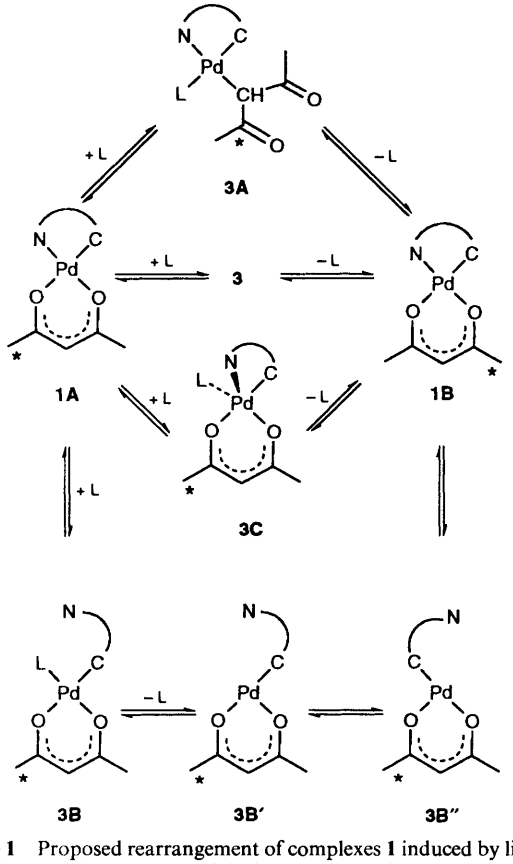


Fig. 4 Accumulation of complex **2b** during irradiation of an acetone solution of complex **1b** (4×10^{-4} mol dm^{-3}) by full light from an 'Osram Ultra Vitalux' lamp in the absence (●) and in the presence of 4×10^{-4} (▼), 8×10^{-4} (■) or 20×10^{-4} mol dm^{-3} (▲) of PPh_3



Scheme 1 Proposed rearrangement of complexes **1** induced by ligands L and the possible structures of the intermediate adducts **3**

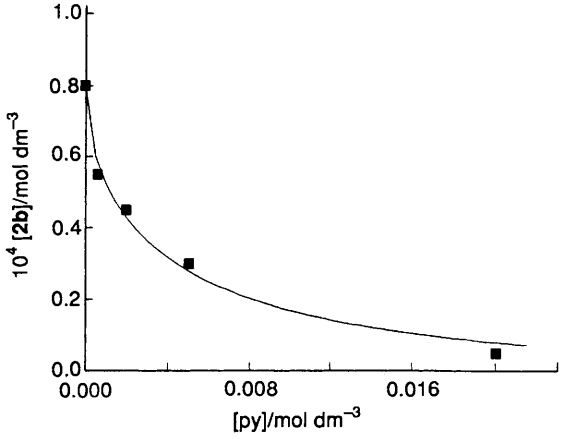


Fig. 5 Plot of concentration of complex **2b** after 15 min of irradiation (200 W tungsten lamp) of an acetone solution of complex **1b** (4×10^{-4} mol dm^{-3}) *versus* concentration of pyridine added

material **1**, and reaction **1** ⟶ **2** starts. When pyridine (py), which is resistant to photooxygenation, is added to a solution of complex **1b** the rate of oxidation decreases (Fig. 5). Adducts **3**, L = py, seem to be weaker in comparison to those with L = PPh_3, because only when a large excess of pyridine is used is the photooxidation of **1b** almost completely inhibited.

We tried to isolate complexes **3** either by crystallization or by chromatography (yellow bands of adducts may be removed with difficulty from silica gel or alumina with polar eluents), but in all cases complexes **1** were recovered instead. However, the changes in the electronic and NMR spectra of complexes **1** upon addition of PPh_3 or pyridine gave preliminary evidence for the formation of the adducts **3**. Thus, addition of PPh_3 to an acetone solution of complex **1b** causes a decrease in the absorption in the region 400–500 nm. Proton and ^{31}P NMR spectra of complex **1b** in chloroform change significantly when PPh_3 is added even when less than the necessary amount to give an adduct is added. Thus, when the ratio **1b**:PPh_3 = 5:1 the methyl protons of the acac ligand appear as a singlet at δ 2.04, intermediate between the values corresponding to **1** (δ 2.12 and 1.99). The methyl of the azo group (δ 2.42 and 2.41), the CH of the acac ligand (δ 5.39) and the aromatic ring protons remain unshifted and some very weak resonances in the regions δ 1.5–2.5 and δ 5.2–6.5 are observed. The main changes in the ^1H NMR spectrum when **1b**:PPh_3 = 2:1 (apart from the obvious changes in the δ 7–8 region) are the growing of those weak peaks observed in the 5:1 spectrum and the shift to lower frequency of one of the methyl protons of the azo group (δ 2.41 and 2.36). In the ^{13}C NMR spectra one singlet (δ 187.4) appears instead of two singlets due to the C=O groups in the spectrum of complex **1b** (δ 186.3 and 188.5) and the methyl groups of the acac ligand become equivalent (δ 27.9 instead of δ 27.6 and 28.1). If the ratio of PPh_3 is increased (**1b**:PPh_3 = 1:2 or 1:3) great changes are then observed. Thus, seven peaks of similar intensity (along with other weak peaks) appear in the δ 1.5–2.8 region and two peaks assignable to the CH proton of the acac ligand are observed at δ 5.5 and 6.4. The ^{31}P NMR spectra of these mixtures show a broad band that shifts to lower frequency, *i.e.* to the region where free PPh_3 is observed, when the amount of PPh_3 is increased. These values are: δ 20.77 (5:1), 15.6 (2:1), 10.4 (1:2) and 6.6 (1:3). Very weak peaks in the δ 26–42 region were also observed. The same occurs when the temperature of the reaction was lowered. Thus, in the reaction **1b** + 3 PPh_3 this band

appears at δ 6.6 (22), 5.6 (0), 5.0 (−10), −0.3 (−20), −4.5 (−30), −5.8 (−40), −6.3 (−50) and −6.6 (−60 °C) while its width decreases. At −60 °C another broad resonance at δ 17.5 and three narrow ones at δ 22.6, 32.2 and 33.4 are observed. All except that at δ 32.2 widen and disappear when the temperature rises. This peak is observed at δ 29.7 at room temperature and could be assigned to Ph_3PO formed during the experiment. The broad resonance at δ 17.5 is observed at δ 18.1 (−50 °C), 18.9 (−40 °C) and at −30 °C disappears. The two others remain unchanged in the range −60 to −40 °C while the δ 22.6 peak starts to broaden at −30 °C and disappears at 0 °C. The same occurs with the one at δ 33.4 at −10 and 22 °C, respectively.

No changes were detected in the ^1H NMR spectrum of complex **1b** at 25 °C when a small amount of pyridine (**1b**:py = 5:1) was added. However, if the concentrations of **1b** and pyridine are comparable, strong broadening of the signals due to the methyl groups of the acac ligand is observed.

It is unfortunate that the isolation of complexes **3** was impossible in our hands, nevertheless, concerning the photochemical process, we may assume that triphenylphosphine taken even in a small amount induces a rapid rearrangement **1A** ⟷ **1B** on the NMR time scale (Scheme 1). In the case of pyridine which forms a less-bound adduct with **1**, it is necessary to add relatively larger amounts of the ligand. Such a rearrangement seems to be possible *via* complex **3**, in which the ligand L is co-ordinated to the palladium ion. A few modes of co-ordination may be considered. Most probably, the co-ordination of L causes the rearrangement of *O,O*- to *C*-acac (structure **3A**). Such a transformation is known for some (acetylacetonato)palladium complexes.[18] The Pd–N bond can also be cleaved by L to give structure **3B**, such as has been observed in some complexes related to **1**.[19] The co-ordinatively unsaturated species **3B′** is produced if L is eliminated from **3B** and its transformation into **3B″** could finally afford **1B**. Lastly, the co-ordination of L to form a five-co-ordinate complex (structure **3C**)[20] in which rapid intramolecular ligand exchange occurs cannot be excluded to explain the NMR spectra. The presence of an excess of L would favour the associative processes leading to a mixture of intermediates (**3A** and/or **3B** and/or **3C**, for example) explaining the ^1H and ^{31}P NMR spectra when the ratio **1b**:PPh_3 = 1:2 or 1:3.

The influence of some other additives on the rate of complex **2b** accumulation was also investigated. Thus, the addition of tetrachloromethane (photoreaction in an acetone–CCl_4 1:3 mixture), which is known to be a scavenger of C-centred free radicals, reduced the rate by approximately four times. Meanwhile, allylbenzene added even in a large excess does not effect the reaction. Water when added to the acetone solution diminished the rate of photooxidation (Fig. 6).

Under the same conditions, complexes **1b** and **1c** are photooxidized in an acetone solution to **2b** and **2c** approximately twice as fast as **1a**, which contains an unsubstituted azobenzene fragment. It may be due to the stronger absorption of **1b** and **1c** in the visible region of spectrum compared to **1a**.

Ketoenolates of cobalt, iron and some other metals are known to be oxygenated upon UV irradiation and were used as initiators of photochemical autooxidation of hydrocarbons.[21] Radicals are believed to be intermediates in these processes. We have, however, found that bis(acetylacetonato)palladium[22] is photochemically inactive under those conditions used for complexes **1**. So, the presence of the azobenzene chromophore fragment in the molecule seems to be a necessary condition to promote photochemical oxygenation of acetylacetonate anions.

A plausible pathway for these processes is shown in Scheme 2. One may assume that in the case of complexes **1** light energy absorbed by the long-wavelength transition of the azobenzene chromophore fragment is intramolecularly transferred to the metal centre. The excited palladium ion is capable of promoting electron transfer from an acetylacetonate ligand and the radical-like acetylacetonyl fragment (structure **A**) thus produced reacts

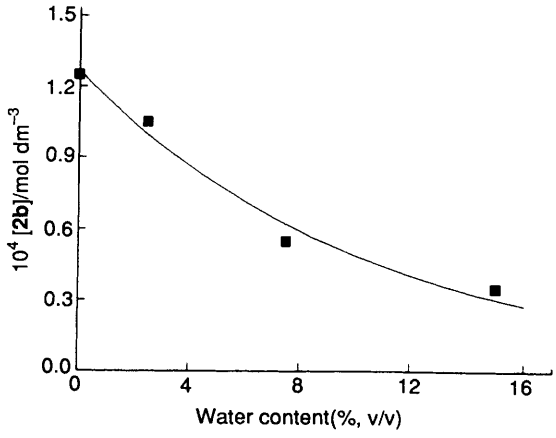
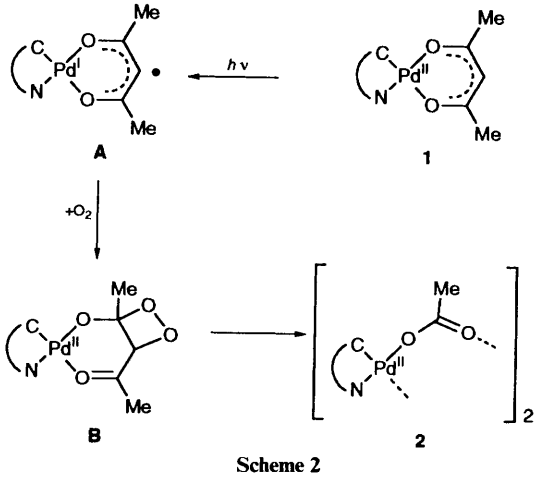


Fig. 6 Plot of concentration of complex **2b** after 5 min of irradiation ('Osram Ultra Vitalux' lamp) of an acetone solution of complex **1b** (5×10^{-4} mol dm^{-3}) *versus* the water content (%, v/v)



Scheme 2

rapidly with molecular oxygen present in the solvent. The palladium(II) complex **B** may be assumed as an intermediate product which decomposes through C–C and O–O bond cleavages (light irradiation could accelerate these processes), giving complexes **2**. If CCl_4 is present in the solution or CH_2Cl_2 is used as solvent, radical **A** may abstract a chlorine atom from CCl_4 or CH_2Cl_2 instead of reacting with molecular oxygen. As a result, the rate of formation of the acetate complex **2** is reduced. In the adducts **3A** and/or **3B**, formed when an excess of L is added (see above), the chromophore and/or the acac ligand change the type of co-ordination present in **1** and, therefore, a disconnection between the chromophore (antenna) and the acac ligand could be responsible for the inhibition of the photochemical oxidation of the acac ligand.

We were unable to detect by mass spectrometry any organic by-product that reasonably could be formed in this reaction (pyruvic acid or pyruvaldehyde, for example). Radical reactions involving molecular oxygen are known to be unselective and to give complex mixtures of products. For example, in the photolysis of (acetylacetonato)cobalt(III), quantities and ratios of organic products were found to vary greatly from one sample to another.[21a] In our case, peroxides could decompose giving oligomerized organic products and/or react with acetone.

In conclusion, complexes **1** are readily oxidized under long-wavelength (even beyond 500 nm) irradiation providing a very simple model of some important chemical and biological photoprocesses. It seems that the sensitivity may be extended into the region of yellow and red light absorption (using, *e.g.* pigment fragments as substituents R in complexes **1**). These results open up ways for the search of related chromophores, metal centres and substrates.

Experimental

The C, H and N analyses, the IR spectra and melting-point determinations were as described elsewhere.[23] The NMR spectra were recorded on Bruker AC200 and Varian Unity 300 spectrometers and the UV/VIS spectra on a Hitachi U-2000 spectrometer. Gas chromatography–mass spectrometry analyses were performed on a HP 5995 spectrometer. Complexes **1** and **2** were prepared as described previously.[24,25]

Photochemical Oxidation.—A solution of complex **1** was irradiated in air in a Pyrex flask (or in a quartz reservoir in the case of spectral determination) which was placed in a Pyrex cylindrical vessel surrounded by a water-cooled (*ca.* 18 °C) jacket. Either water or aqueous inorganic salt solutions as light filters were placed in this vessel.

The following sources of light were used to illuminate a 3×10^{-4} mol dm^{-3} solution of **1b** (wavelength in nm and relative initial rate of **2b** accumulation are given in parentheses): 250 W medium-pressure mercury arc in a Pyrex vessel ($\lambda > 300$, 1.0); sunlight for solutions in a quartz reservoir ($\lambda > 270$, 0.8); 300 W tungsten lamp combined with weak mercury arc ('Osram Ultra Vitalux') in a Pyrex vessel ($\lambda > 300$, 0.7) [$\lambda > 420$, 0.4 with an aqueous $K_4Fe(CN)_6$ filter or $\lambda > 500$, 0.2 with an aqueous Na_2CrO_4 filter]; 200 W standard tungsten lamp ($\lambda > 400$, 0.1) (see text and figure captions).

Acknowledgements

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