Some Alkyldiplatinum(I) Complexes and Studies of the Photochemical and Thermal Decomposition of the $[Pt_2Et(\mu\text{-}Ph_2PCH_2PPh_2)_2(Ph_2PCH_2PPh_2\text{-}P)]^+$ Cation†

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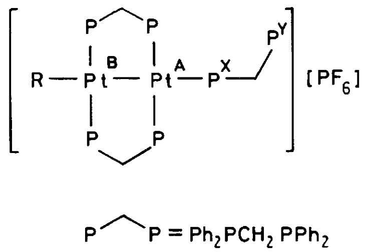
The first alkyldiplatinum(I) complexes containing β-hydrogen atoms, $[Pt_2R(\mu\text{-dppm})_2(\text{dppm-}P)][PF_6]$ (R = Et, CD_3CH_2, Pr, or Bu; dppm = $Ph_2PCH_2PPh_2$), were prepared by reaction of $[Pt_2(\mu\text{-dppm})_3]$ with RI followed by addition of $K[PF_6]$. The complexes were yellow, air-stable solids which were characterized by ^1H and ^{31}P n.m.r. spectroscopy. Photochemical or thermal decomposition of the ethyl derivative was shown to involve β elimination, which occurred subsequent to the rate-determining step.

Binuclear platinum complexes with bridging ligands $Ph_2PCH_2PPh_2$ (dppm) have given useful models for catalytic intermediates.[1] One desirable functional group is an alkylplatinum unit in a complex with a Pt–Pt bond which represents a very crude model of an alkyl group on a platinum surface.[2] In this paper the synthesis of such complexes, in which the alkyl groups are ethyl, propyl, or butyl, is reported. The thermally and photochemically induced β elimination of ethylene from the ethyldiplatinum complex has also been studied.



	R
(1a)	Me
(1b)	Et
(1c)	CH_2CD_3
(1d)	Pr
(1e)	Bu
(1f)	H
(1g)	D

Results and Discussion

Synthesis and Characterization of New Complexes.—The new alkyldiplatinum(I) complexes $[Pt_2R(\mu\text{-dppm})_2(\text{dppm-}P)][PF_6]$ were prepared by reaction of the appropriate alkyl iodide, RI, with $[Pt_2(\mu\text{-dppm})_3]$ in benzene, followed by treatment with excess of the bulky anion $[PF_6]^-$. The synthesis is thus essentially the same as that used previously to prepare complex (**1a**) from methyl iodide and $[Pt_2(\mu\text{-dppm})_3]$,[2] but the new reactions were much slower. Reaction with a stoicheiometric amount of methyl iodide was complete in 3.5 h at room temperature, but reaction with ethyl iodide took 18—20 h to reach completion; propyl and butyl iodides reacted still more slowly. Attempts to prepare similar derivatives (1) from $[Pt_2(\mu\text{-dppm})_3]$ and CF_3I, Pr^iI, Bu^tI, $CH_2{=}CHCH_2I$, PhI, or $PhCH_2Br$ were unsuccessful; the only products characterized were $[Pt_2X_2(\mu\text{-dppm})_2]$, X = I or Br.

Complexes (**1b**)—(**1e**) are yellow, air-stable solids which were characterized by elemental analysis and ^1H and ^{31}P n.m.r. spectroscopy. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were very similar to those of the known methyl and hydrido-derivatives (**1a**) and (**1f**) respectively,[2–4] and the parameters are given in the Experimental section. At room temperature, the ^{31}P signals due to the dppm-*P* ligand were broad due to the onset of exchange between the phosphorus atoms P^X and P^Y in structure (1), but sharp signals with well resolved $^2J(P^XP^Y)$ couplings were observed at low temperature.

The ^1H n.m.r. spectrum of complex (**1b**) was of some interest. At room temperature, single resonances were observed for the CH_3[δ −0.61, ^3J(PtH) 52 Hz] and CH_2 (δ 0.65) protons of the ethyl group, and for the different CH_2P_2 protons of the μ-dppm (δ 5.1) and dppm-*P* (δ 2.0) groups. However at −40 °C, two separate resonances were observed for the CH_2 protons of the ethyl group (δ 0.56 and 0.72)and also for the CH_2P_2 protons of the dppm-*P* ligand (δ 1.30 and 2.70). The signal due to the CH_2P_2 protons of the μ-dppm ligands became exceedingly broad at −40 °C. These results indicate that (**1b**) adopts a locked-in conformation, in which there is no plane of symmetry containing either the CCPt atoms of the ethylplatinum group or the PtPCP atoms of the dppm-*P* group. It is probable that the dppm-*P* ligand is in a similar conformation to that found in the solid-state structure of (**1f**).[3] Very similar effects to those for complex (**1b**) were observed in the variable-temperature ^1H n.m.r. spectra of (**1e**).

Photochemistry of Complexes (**1b**) *and* (**1c**).—Photolysis of complex (**1b**) in degassed acetone solution using 500-nm incident light led to decolourization of the initially yellow solution. The reaction was monitored by spectrophotometry using the decay of the absorption band at 466 nm due to (**1b**) (Figure 1) to determine the rate of disappearance of this complex. At the end of the reaction (using light with λ >510 nm), g.c. analysis showed the formation of C_2H_4 [0.80 mol per mol (**1b**) decomposed] and C_2H_6 [0.20 mol per mol (**1b**)

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† Bis[μ-bis(diphenylphosphino)methane-*PP′*]-1-[bis(diphenylphosphino)methane-*P*]-2-ethyldiplatinum(I) (*Pt–Pt*).

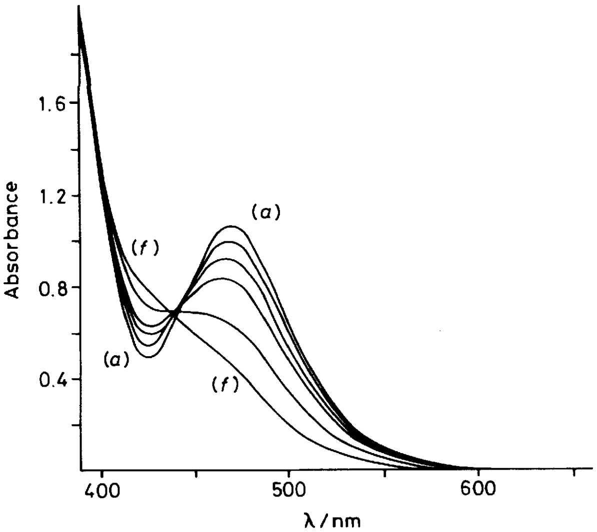


Figure 1. Changes in the u.v.–visible spectrum on photolysis (λ >500 nm) of complex (**1b**) in acetone. Spectra (*a*)—(*f*) were recorded at photolysis times 0, 11, 25, 40, 70, and 110 min

decomposed]. The platinum-containing product was identified by i.r. and ^{31}P n.m.r. spectroscopies as (**1f**), but the maximum yield was only 65% as determined by quantitative measurement of the ν(PtH) band at 2 010 cm^{-1} due to (**1f**).

The primary reaction is almost certainly a β elimination[5] of ethylene from complex (**1b**) to give C_2H_4 and (**1f**). A further photochemical reaction then occurs between (**1f**) and (**1b**) to give C_2H_6 and platinum-containing products which could not be identified. Evidence for this sequence was obtained as follows. Irradiation of complex (**1b**) at 473 nm, where (**1f**) absorbs relatively more strongly than at 500 nm, led to an increase in the yield of ethane to 0.25 mol per mol (**1b**) decomposed, and irradiation of an equimolar mixture of (**1b**) and (**1f**) led to a further increase in ethane yield to 0.35 mol per mol (**1b**) decomposed.

The β elimination reaction was shown to occur after the rate-determining step by the following experiment. Proton n.m.r. analysis of a mixture obtained by photolysis of a solution of complex (**1c**) in CD_3CN to *ca.* 50% conversion showed no scrambling of label in (**1c**) to give units such as $PtCD_2CH_2D$,[5] which would be formed if the β elimination was reversible. It is unlikely that β elimination is the rate-determining step since there was not a significant isotope effect on the quantum yield for decomposition of (**1b**) *vs.* (**1c**) (Figure 2). The quantum yields were low [$(5.3 \pm 0.5) \times 10^{-4}$ at 500 nm, $(6.5 \pm 0.5) \times 10^{-4}$ at 473 nm] and were not affected by photolysis in the presence of free dppm. Since the β elimination is not rate determining and does not precede the rate-determining step, it must occur after this step.

The quantum yield for photolysis of $[Pt_2Et_3(\mu\text{-dppm})_2]^+$ was much higher ($\varphi > 0.5$)[6] and initially gave C_2H_4 and $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, which then underwent further efficient photolysis to give C_2H_6 and unidentified platinum-containing products. The latter reaction is similar to the known photolysis of $[Pt_2Me_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ to give methane,[7,8] but photolysis of $[Pt_2Me_3(\mu\text{-dppm})_2]^+$ occurs efficiently with carbon–carbon bond coupling to give ethane.[8] None of the analogous product butane was formed on photolysis of $[Pt_2Et_3(\mu\text{-dppm})_2]^+$.

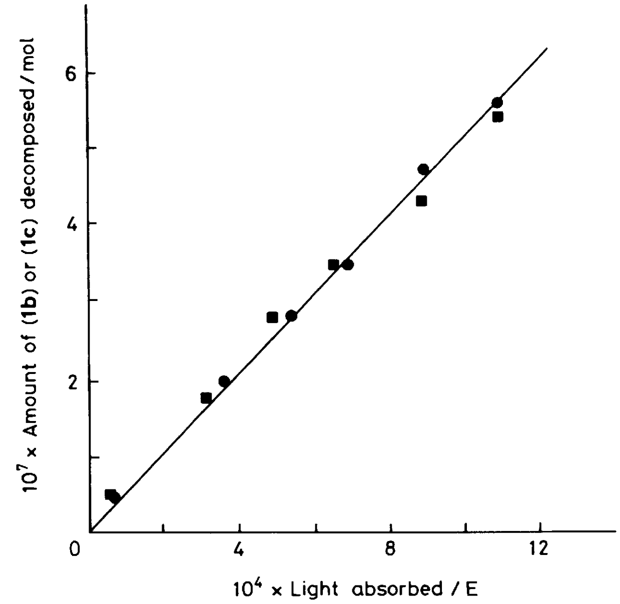


Figure 2. Plot of moles of complex (**1b**) (circles) or (**1c**) (squares) decomposed *vs.* Einsteins of light (λ 500 nm) absorbed by each complex

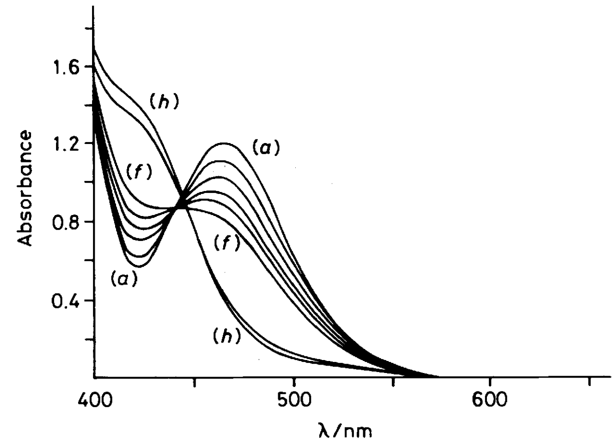


Figure 3. Changes in the u.v.–visible spectrum on thermolysis of complex (**1b**) in acetonitrile at 100 °C. Spectra (*a*)—(*h*) were recorded at thermolysis times 0, 123, 213, 314, 416, 510, 1 970, and 3 160 min

Thermolysis of Complexes (**1b**) *and* (**1c**).—The complex (**1b**) was surprisingly robust but thermolysis occurred at a measurable rate at temperatures from 60 to 100 °C in acetonitrile or dimethyl sulphoxide solvents. The decomposition was much faster in the presence than in the absence of air, and so thermolyses were conducted using rigorously degassed solutions. The gaseous products from thermolysis of (**1b**) in CH_3CN solution were C_2H_4 and C_2H_6 in approximately a 2:1 molar ratio, suggesting initial β elimination.[5] However, the expected product (**1f**) was not formed and the platinum-containing products could not be characterized. Independent study showed that complex (**1f**) decomposed faster than (**1b**) and gave the same products, as shown by the ^{31}P n.m.r. spectra. It is likely therefore that (**1f**) is the initially formed product but that it decomposes too rapidly to allow identification.

As in the photolysis, partial thermolysis of complex (**1c**) did not lead to scrambling of the deuterium label within the $[^2H_3]$ethylplatinum group of unreacted (**1c**), nor was there a significant isotope effect on the rate of thermolysis. These results indicate that the rate-determining step precedes the β-elimination step.[5] The ratio of ethylene:ethane was the same for (**1c**) as for (**1b**) as determined by g.c. analysis.

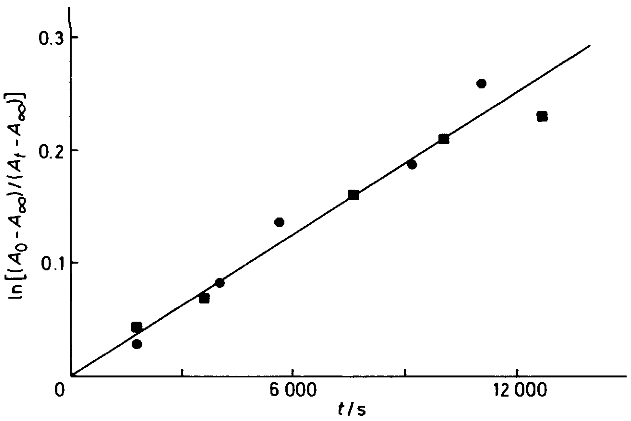


Figure 4. First-order plot for thermolysis of complex (**1b**) (circles) or (**1c**) (squares) in acetonitrile at 100 °C

The thermolyses of complexes (**1b**) and (**1c**) followed first-order kinetics to at least one half-life. After this time the isosbestic point in the u.v.–visible spectra was lost and a more complex kinetic behaviour resulted (Figures 3 and 4). The rate of thermolysis is not affected by the presence of free dppm.

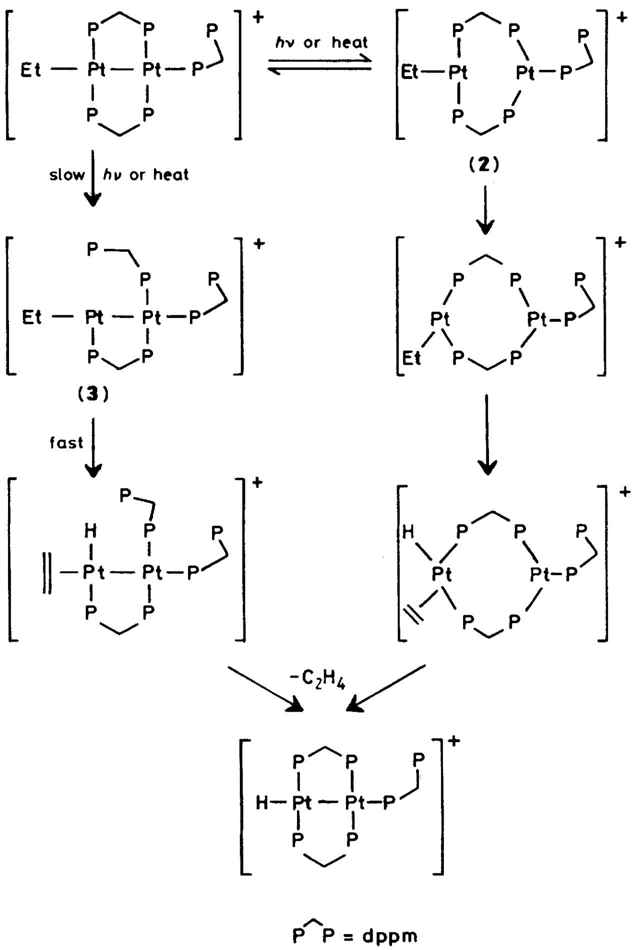
Conclusions

It is clear from these results that the presence of the Pt–Pt bond in complex (**1b**) does not lead to activation towards β elimination. The complexes are decomposed only slowly by thermal or photochemical activation. There is insufficient evidence to determine the detailed mechanism of reaction. However, in both the thermal and photochemical reactions it seems that a slow step occurs to give an intermediate from which rapid β elimination occurs. One possible sequence of reactions is shown in the Scheme. It is probable that the fastest step involves reversible cleavage of the metal–metal bond to give complex (**2**) [this could occur homolytically to give two platinum(I) fragments or heterolytically to give a Pt^0–Pt^{II} species], but this does not lead to a vacant site *cis* to the ethyl group as required for β elimination.[5,9] Eventually, phosphine dissociation occurs to give (**3**), with a *cis* vacant site, and then rapid β elimination follows. This accounts for the low quantum yield in the photochemical reaction and the low rate, similar to that for decomposition of *cis*-[PtEt$_2$(PEt$_3$)$_2$] *via* phosphine dissociation,[10] in the thermal decomposition. The lack of retardation by free dppm is not inconsistent with this mechanism but, as in other studies of β elimination in binuclear systems,[5,11] the evidence is by no means definitive. For example, it is possible that further rearrangement of complex (**2**) could give another intermediate from which β elimination could occur.

Experimental

General techniques have been described previously.[2,4,6–8] N.m.r. spectra were recorded using Varian XL100, Bruker WM250, and Bruker WP400 spectrometers. Chemical shifts are quoted with respect to SiMe$_4$(^{1}H) or phosphoric acid (^{31}P). The complexes [Pt$_2$Et$_3$(μ-dppm)$_2$][PF$_6$] and [Pt$_2$Et$_2$(μ-H)(μ-dppm)$_2$][PF$_6$] were prepared by the literature methods.[6]

Preparations.—[Pt$_2$R(dppm)$_3$][PF$_6$] (R = Et, Pr, *or* Bu). These complexes were prepared from pure [Pt$_2$(dppm)$_3$][12] by procedures similar to that used for the methyl complex[2] except that longer reaction times (18—20 h) were necessary. Preparations of the propyl and butyl complexes required the use of more than the stoicheiometric amount of the corresponding iodoalkane because of slower reaction rates. Exchange of I$^-$ for [PF$_6$]$^-$ was effected by the use of K[PF$_6$] (5 mol equiv.) in aqueous solution as described above.



Scheme.

The complex [Pt$_2$(dppm)$_3$] (3.58 g, 2.32 mmol), iodoethane (0.362 g, 2.32 mmol), and benzene (16 cm^3) gave [Pt$_2$Et(dppm)$_3$][PF$_6$] (2.59 g, 65%), which was recrystallized from dichloromethane {Found: C, 53.4; H, 4.1; Cl, 1.3; F, 6.9; P, 12.1. Calc. for [Pt$_2$Et(dppm)$_3$][PF$_6$]·0.3CH$_2$Cl$_2$: C, 53.4; H, 4.1; Cl, 1.2; F, 6.5; P, 12.4%}. N.m.r. (CD$_2$Cl$_2$): ^{1}H (20 °C) δ − 0.61 [3 H, t, ^3J(PtH) 52, CH$_3$C], 0.65 (2 H, br, CH$_2$Pt), 2.0 (2 H, br, dppm-*P*), and 5.10 (4 H, br, dppm-*PP′*); (−40 °C), −0.61 [3 H, t, ^3J(PtH) 52, CH$_3$C], 0.56 and 0.72 (2 H, br, CH^{A}H^{B}Pt), 1.30 and 2.70 (2 H, m, br, CH^{A}H^B of dppm-*P*); ^{31}P, −25.5 (br, P^Y), 6.46 [m, ^1J(PtP) 3 170, P^A], 14.93 [m, ^1J(PtP) 3 612 Hz, *N* 80 Hz, P^B], and 23.7 (m, P^X).

The complex [Pt$_2$(dppm)$_3$] (0.733 g, 0.475 mmol), iodopropane (0.323 g, 1.89 mmol), and benzene (8 cm^3) gave [Pt$_2$Pr(dppm)$_3$][PF$_6$] (0.482 g, 59%) {Found: C, 54.3; H, 4.4; Cl, <0.1; P, 12.4. Calc. for [Pt$_2$Pr(dppm)$_3$][PF$_6$]: C, 54.1; H, 4.3; P, 12.5%}. N.m.r. (CD$_2$Cl$_2$): ^{31}P, δ −25.8 (br, P^Y), 6.49 [m, ^1J(PtP) 3 164, P^A], 15.02 [m, ^1J(PtP) 3 652 Hz, *N* 80 Hz, P^B], and 23.7 (m, P^X).

The complex [Pt$_2$(dppm)$_3$] (1.05 g, 0.680 mmol), iodobutane (0.626 g, 3.40 mmol), and benzene (10 cm^3) gave [Pt$_2$Bu(dppm)$_3$][PF$_6$] (0.67 g, 58%) {Found: C, 54.5; H, 4.3. Calc. for [Pt$_2$Bu(dppm)$_3$][PF$_6$]: C, 54.4; H, 4.3%}. N.m.r.

(CD_2Cl_2): ^1H (20 °C), δ -0.58 (2 H, CH^{β}_2), -0.26 (2 H, CH^{γ}_2), -0.18 (3 H, CH_3), 0.57 (2 H, CH^{α}_2), and 2.07 (2 H, br, dppm-*P*); (-73 °C), -0.98 (2 H, CH^{β}_2), -0.67 (2 H, CH^{γ}_2), -0.27 (3 *H*, CH_3), 0.44 (2 H, CH^{α}_2), 1.12 and 2.76 (2 H, CH^AH^B of dppm-*P*), and *ca.* 5 (4 H, br, dppm-*PP′*); ^{31}P, -26.0 (br, P^Y), 6.63 [m, ^1J(PtP) 3 174, P^A], 15.26 [m, ^1J(PtP) 3 656 Hz, *N* 83 Hz, P^B], and 23.7 (m, P^X).

$[Pt_2(CH_2CD_3)(dppm)_3][PF_6]$. A similar reaction of $[Pt_2(dppm)_3]$ (2.08 g, 1.35 mmol) with CD_3CH_2I (0.300 g, 1.89 mmol) in benzene (12 cm^3) at 20 °C for 28 h followed by treatment of the product with $K[PF_6]$ gave $[Pt_2(CH_2CD_3)(dppm)_3][PF_6]$ (0.926 g, 44%). This was characterized by its ^1H and ^{31}P n.m.r. spectra, by comparison with those of complex (**1b**). The resonance in the ^1H n.m.r. spectrum of (**1b**) at δ -0.61 was absent.

Reactions of $[Pt_2(dppm)_3]$.—*With benzyl bromide.* Freshly distilled benzyl bromide (0.58 g, 3.4 mmol) and $[Pt_2(dppm)_3]$ (0.797 g, 0.516 mmol) in benzene (20 cm^3) were allowed to react at 20 °C for 2 h. The yellow solid thus obtained was recovered by filtration, washed with benzene and cyclohexane, and dried. It was shown by ^{31}P n.m.r. spectroscopy to be almost pure $[Pt_2Br_2(\mu\text{-dppm})_2]$ (0.542 g, 80%). No resonances characteristic of a $[Pt_2R(dppm)_3]^+$ species could be observed.

With allyl iodide. Allyl iodide (0.16 g, 0.95 mmol) and $[Pt_2(dppm)_3]$ (0.369 g, 0.239 mmol) in benzene (7 cm^3) were allowed to react at 20 °C for 2 h. The bright yellow product (0.328 g), isolated as above, was recrystallized from dichloromethane and cyclohexane to afford pure $[Pt_2I_2(\mu\text{-dppm})_2]$ (0.228 g, 68%) identified by its ^{31}P n.m.r. spectrum.

With some other organic iodides. The reactions of trifluoroiodomethane, 2-iodopropane, 2-iodo-2-methylpropane, and iodobenzene with $[Pt_2(dppm)_3]$ in benzene were examined in a similar way. In every case the solid product separating from solution consisted of impure $[Pt_2I_2(\mu\text{-dppm})_2]$ and ^{31}P n.m.r. spectra failed to reveal the presence of $[Pt_2R(dppm)_3]^+$ species.

Thermolysis of Degassed Solutions of $[Pt_2Et(dppm)_3][PF_6]$.—A sample of $[Pt_2Et(dppm)_3][PF_6]$ (0.0071 g) was dissolved in acetonitrile (5.0 cm^3), degassed, and flame sealed into a quartz-faced cuvette. The visible absorption spectrum was recorded. The sample was then placed in a bath at 100 °C. Periodically the sample was removed, cooled to room temperature, and the absorption spectrum recorded. In the early stages (approximately one half-life), an isosbestic point was evident at 442 nm (Figure 3). First-order analysis of the data gave a rate constant of $(2.2 \pm 0.3) \times 10^{-5}$ s^{-1} for decomposition of $[Pt_2Et(dppm)_3]^+$.

Identical experiments were conducted with $[Pt_2(CH_2CD_3)(dppm)_3][PF_6]$. In this case, additional experiments were carried out in the presence of dppm and $[Pt_2D(dppm)_3][PF_6]$. When these additives were used, they were mixed with $[Pt_2(CH_2CD_3)(dppm)_3][PF_6]$ prior to dissolution. The first-order rate constants (k_1/s^{-1}) at 100 °C were: no additive, $(2.0 \pm 0.3) \times 10^{-5}$; [dppm] $= 7.8 \times 10^{-3}$ mol dm^{-3}, $(2.0 \pm 0.3) \times 10^{-5}$; $[Pt_2D(dppm)_3][PF_6] = 9 \times 10^{-4}$ mol dm^{-3}, $(1.8 \pm 0.3) \times 10^{-5}$.

Thermolysis was also conducted and monitored by n.m.r. spectroscopy. In this case a sample of $[Pt_2(CH_2CD_3)(dppm)_3][PF_6]$ (0.0813 g) in $[^2H_3]$acetonitrile (0.8 cm^3) was degassed and flame sealed in a 5-mm n.m.r. tube. The sample was then heated to 100 °C. The ^1H n.m.r. spectrum was run periodically and the loss of intensity of the resonance due to the Pt–CH_2 protons was observed [$\delta = 0.53$, $^2J(PtH) = 58$, $^3J(PP) = 7.5$ Hz]. Throughout the reaction, no resonance due to the methyl group ($PtCH_2CH_3$) was observed.

Upon completion of the reaction, the ^{31}P n.m.r. spectrum was obtained and found to contain resonances due to an unknown species which gave an $[A_2B_2]$ multiplet, with ^{195}Pt satellites. The product had the following ^{31}P spectral parameters: δ 2.0 [^1J(PtP) 3 120, P^A], and 5.5 [^1J(PtP) 3 050 Hz, P^B]. The tube was then opened and the gas phase was analysed by g.c. and found to contain ethylene and ethane in a 2:1 molar ratio.

Thermolysis of an identically prepared sample of $[Pt_2H(dppm)_3][PF_6]$ gave rise to identical platinum-containing products as determined from the $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum. However, no gas was produced.

Photolysis of $[Pt_2Et(dppm)_3]^+$.—A sample of $[Pt_2Et(dppm)_3][PF_6]$ (0.097 g) in acetone (10 cm^3) was degassed and flame sealed into a Pyrex vessel attached to a quartz optical cell (pathlength 1 mm). The sample was irradiated with a 150-W xenon lamp placed 25 cm from the sample. The output of the lamp was filtered by placing a filter (Corning 3-73, band pass $\lambda > 410$ nm) between it and the sample. The sample was removed periodically and the visible absorption spectrum was obtained. After 5 h, no further change in the absorption was observed. The sample was then opened and the solvent removed under vacuum. The product (0.08 g) was then dissolved in CH_2Cl_2 and the i.r. spectrum was obtained. An absorption at ν(PtH) 2 010 cm^{-1} was identified as due to $[Pt_2H(dppm)_3]^+$ by comparison with the i.r. spectrum of an authentic sample. By measuring the intensity of this absorption the product mixture was found to contain 25% $[Pt_2H(dppm)_3][PF_6]$.

The experiment was then repeated with a new filter (Corning 3-70), such that only light of $\lambda > 510$ nm was passed to the sample. In this case the final product was found to contain 65% $[Pt_2H(dppm)_3][PF_6]$.

In a similar experiment, a sample of $[Pt_2Et(dppm)_3][PF_6]$ (0.019 g) in acetone (2 cm^3) was degassed and photolysed (using the Corning 3-70 filter). The reaction was monitored by observing changes in the visible absorption spectrum. At 66% completion of reaction, the reaction was stopped. The gas was analysed and found to contain 0.80 mol of ethylene and 0.20 mol of ethane per mol $[Pt_2Et(dppm)_3][PF_6]$ decomposed. This experiment was repeated with a mixture of $[Pt_2Et(dppm)_3][PF_6]$ (0.011 g) and $[Pt_2H(dppm)_3][PF_6]$ (0.010 g). The ratio of ethane to ethylene produced was found to be 0.50:1. A sample of $[Pt_2(CH_2CD_3)(dppm)_3][PF_6]$ was degassed and flame sealed in a 5-mm n.m.r. tube. The sample was irradiated as above and the ^1H n.m.r. spectrum was obtained periodically. The signal due to the Pt–CH_2 group was found to decrease. During the course of the reaction no signal due to $PtCH_2CH_3$ was observed.

Quantum-yield determinations. In a typical experiment, $[Pt_2Et(dppm)_3][PF_6]$ (0.0207 g) was dissolved in acetonitrile (10.0 cm^3). A portion of this solution (4.0 cm^3) was then degassed and flame sealed into a quartz cuvette (pathlength 1.0 cm).

The sample was then irradiated with the Jasco CRM-FA spectroirradiator. The intensity of the band used (500 ± 4 nm) had been calibrated by actinometry, using $K_3[Fe(C_2O_4)_3]$. The extent of reaction and hence the concentration of $[Pt_2Et(dppm)_3]^+$ was monitored by measuring the optical density at 466 nm, and quantum yields were obtained as described previously[13] and outlined below. Plots of the moles of $[Pt_2Et(dppm)_3]^+$ decomposed *vs.* moles of light absorbed by this complex were linear, giving a slope equal to the quantum yield, $(5.3 \pm 0.5) \times 10^{-4}$. The quantum yield for decomposition of $[Pt_2(CH_2CD_3)(dppm)_3]^+$ under identical conditions was found to be $(5.2 \pm 0.5) \times 10^{-4}$. The difference is not significant.

The quantum yield for decomposition of $[Pt_2Et(dppm)_3]^+$ in 0.066 mol dm^{-3} dppm was found to be $(5.5 \pm 0.5) \times 10^{-4}$. In a similar manner, quantum yields for the decomposition of $[Pt_2Et(dppm)_3]^+$ and $[Pt_2(CH_2CD_3)(dppm)_3]^+$ were measured using 473 ± 4 nm light and found to be (6.4 ± 0.5) × 10^{-4} and (6.6 ± 0.5) × 10^{-4} respectively.

Photolysis of $[Pt_2Et_3(\mu\text{-dppm})_2]^+$.—A sample of $[Pt_2Et_3(\mu\text{-dppm})_2][PF_6]$ (0.05 g) was dissolved in CD_2Cl_2 (1 cm^3) in a 5-mm n.m.r. tube. It was then irradiated with the filtered output from a medium-pressure mercury lamp. The sample was placed 12 cm from the lamp and two filters (water and λ >420 nm) were interposed between the lamp and sample. After 10 min of irradiation, a sample of the gas above the liquid was analysed by g.c. (Porapak Q column) and found to contain 75 ± 10% C_2H_4 and 25 ± 10% C_2H_6. The ^{31}P n.m.r. spectrum of the solution contained peaks due to the starting material (*ca.* 55%), $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (*ca.* 44%), and an unidentified compound (*ca.* 1%).

The gas was then removed by a stream of N_2 and the procedure was repeated, this time photolysing the solution for 1 h. The gas-analysis results obtained were now 50% C_2H_4 and 50% C_2H_6. The ^{31}P n.m.r. spectrum indicated that no starting material remained and the products were $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$ (*ca.* 55%) and the unidentified compound (45%).

The experiment was repeated under degassed conditions to yield, after 40 min of irradiation, 25% $[Pt_2Et_3(\mu\text{-dppm})_2]^+$, 64% $[Pt_2Et_2(\mu\text{-H})(\mu\text{-dppm})_2]^+$, and 11.0% of the new complex. The gas analysis indicated C_2H_4 (75%) and C_2H_6 (25%). The unidentified platinum complex had δ(P) 11.8 [^1J(PtP) 3 320 Hz].

Acknowledgements

For financial support we thank the N.S.E.R.C. (Canada) and the S.E.R.C. (U.K.).

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Received 11*th February* 1985; *Paper* 5/235