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Photochemistry of mononuclear and binuclear tetramethylplatinum(IV) complexes: reactivity of an organometallic free radical *

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Abstract

Photolysis of $[PtMe_4(bipy)]$, bipy = 2,2′-bipyridine, gives homolysis of one of the mutually trans methyl–platinum bonds. In the presence of chlorinated solvents, the platinum-containing product is $[PtClMe_3(bipy)]$ and the quantum yield in CH_2Cl_2 is 0.96. The reaction is quenched by the triplet quencher perylene. Direct evidence for methyl radical formation includes spin trapping of methyl radicals and CIDNP experiments. Novel photochemical reactions include those with RCCH and RCO_2Me to give $[Pt(CCR)Me_3(bipy)]$ and $[Pt(O_2CR)Me_3(bipy)]$, respectively. The binuclear complexes $[Pt_2Me_8(\mu\text{-bipym})]$ and $[Pt_2Me_6(\mu\text{-bipym})]$, bipym = 2,2′-bipyrimidine, are much less photosensitive. The former reacts in chloroform solution to give $[Pt_2Cl_2Me_6(\mu\text{-bipym})]$ while the latter undergoes disproportionation to give $[Pt_2Me_8(\mu\text{-bipym})]$ and $[Pt_2Me_4(\mu\text{-bipym})$. Labelling studies indicate that this reaction occurs by dissociation of a bidentate ligand from platinum.

Introduction

Photolysis of alkyl complexes of transition metals usually leads to α- or β-elimination reactions or to homolysis of a transition metal–alkyl bond [1,2]. Free radical reactions are of fundamental importance throughout organometallic chemistry and so efficient metal–carbon bond homolysis by photolysis is potentially useful in synthesis [3,4]. Photolysis of alkylplatinum(II) and alkylplatinum(IV) complexes has been studied previously and evidence for alkyl radical formation has been presented in several cases [2,5–8]. This paper describes details of the photochemistry of the complex $[PtMe_4(bipy)]$, bipy = 2,2′-bipyridine (**1**) [9–11], which occurs with high quantum yield, and of two binuclear tetramethylplatinum(IV) complexes which are much less photosensitive. A preliminary account of parts of this work has been published [12].

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* Dedicated to Professor Alwyn G. Davies, from whom the excitement of discovery is so readily learned, in recognition of his many distinguished contributions to organometallic chemistry.

Results

The absorption spectrum of [PtMe$_4$(bipy)]

Complex **1** is orange-red in color whereas most alkylplatinum(IV) complexes are colorless or pale yellow. The absorption maximum for the lowest energy band in the UV-visible absorption spectra of complexes [PtMe$_4$(bipy)] and [PtMe$_2$(bipy)] [13] in solvents of different polarity are given in Table 1. It can be seen that for both complexes there is a marked red shift in solvents of lower polarity and this feature is commonly observed for metal to ligand charge transfer (MLCT) bands [14]. For [PtMe$_2$(bipy)], the band has been assigned to a Pt(5*d*)-bipy(π^*) transition [13]. A similar assignment is clearly possible for [PtMe$_4$(bipy)] but the non-bonding 5*d* orbitals (t_{2g}) in platinum(IV) complexes are usually too low in energy to give such MLCT bands in the visible region of the spectrum (thus, for example, complexes [PtXMe$_3$(bipy)], X = halogen, are colorless or pale yellow and have no absorption maximum over 350 nm) and so other assignments should be considered. In late transition elements, two mutually *trans* alkyl groups have a destabilizing effect on each other (antisymbiosis [15]) and have a high energy σ(M–C) orbital. Hence the UV-visible transition could be due to a σ(M–C)–π^*(bipy) transition. Such transitions can certainly occur in the visible, as for example in dialkyl(2,2′-bipyridine)beryllium(II) complexes for which no other assignment is reasonable [16]. Complex **1** failed to give detectable emission either at room temperature in the solvents given in Table 1 or in an ether glass at 77 K and so no extra insight about the excited state can be obtained. The assignment as σ(M–C)–π^*(bipy) is most consistent with the photochemistry described below, but is not proved.

Photochemical reactions of [PtMe$_4$(bipy)]

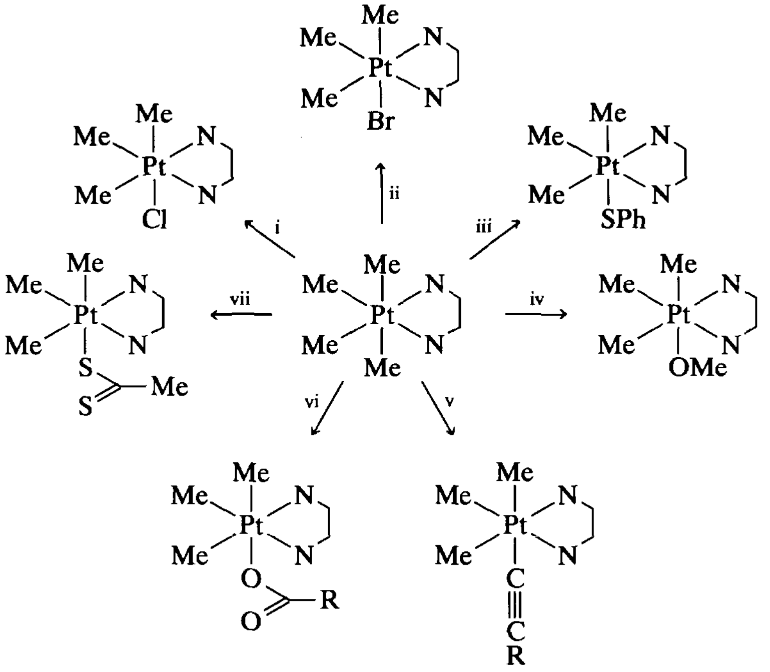
The photochemical reactions are summarized in Scheme 1. Photolysis of **1** ($\lambda > 420$ nm) in either $CHCl_3$ or CH_2Cl_2 gave [PtClMe$_3$(bipy)] and methane. The progress of the reaction could be monitored easily by UV–VIS absorption spectroscopy as shown in Fig. 1. The absorption band at 456 nm due to **1** decayed as the reaction proceeded. The photolysis of **1** in acetone containing excess $BrCH_2$-CH_2Br proceeded similarly to give [PtBrMe$_3$(bipy)], but a mixture of organic products including CH_4, CH_3Br and C_2H_6 was formed in this case.

Table 1

The UV–VIS absorption spectra (λ_{max}, nm) of complexes **1**, [PtMe$_2$(bipy)] = **2**, **3** and **4** as a function of solvent polarity

Solvent	E_T [a]	**1**	**2**	**3**	**4**
Acetone	42.2	441	461	555	556
Pyridine	40.2	449			
Methanol		449			
Dichloromethane	41.1	456	458	583	563
Tetrahydrofuran	37.4	458		570	582
Benzene	34.5	475	489	590	600
Diethyl ether		475		625	612
Toluene	33.9	477	494	600	608
Carbon disulfide		509		652	640

[a] The Reichardt parameter of solvent polarity.



Scheme 1. Reagents are *hν* and (i) $CHCl_3$ or CH_2Cl_2; (ii) $C_2H_4Br_2$; (iii) PhSH; (iv) MeOH; (v) RCCH, R = Me, CH_2CH_2OH or Ph; (vi) RCO_2Me, R = H, Me or MeO_2CCC; (vii) CS_2.

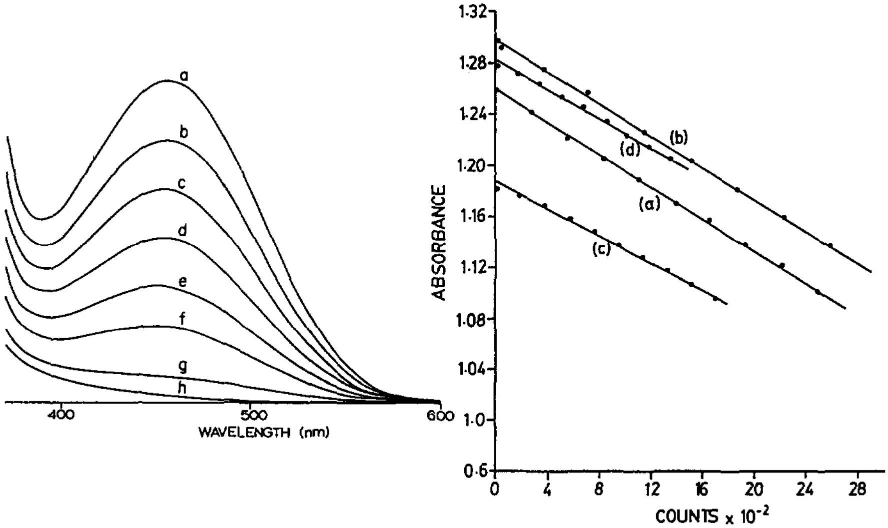


Fig. 1. Left: Electronic spectral changes during the 473 nm photolysis of [$PtMe_4$(bipy)] in CH_2Cl_2. Total irradiation in counts: (a) 0; (b) 1; (c) 2; (d) 3; (e) 4; (f) 5; (g) 7; (h) 15. Right: Graphs of absorbance *vs.* light absorbed for the photolysis of [$PtMe_4$(bipy)] in (a) CH_2Cl_2; (b) acetone; (c) deoxygenated $CHCl_3$; (d) MeOAc.

Complex **1** reacts thermally with PhSH to give methane and [Pt(SPh)Me_3(bipy)] [11] but the photochemical reaction (Scheme 1), which gives the same products, is much faster and so can be studied separately. Carbon disulfide fails to react with **1** thermally, but the photochemical reaction occurs readily to give [Pt(S_2CMe)Me_3(bipy)] by insertion of CS_2 into a Pt–Me bond. The product is a new complex, which was readily identified by its ^{1}H NMR spectrum, which contained three methyl resonances in a 2 : 1 : 1 ratio. The first is due to the two methyl groups *trans* to bipy and has ^2J(PtH) = 70 Hz, the second is due to the MePt group *trans* to the dithioacetate group and has ^2J(PtH) = 59 Hz, while the third is due to the dithioacetate group and has ^4J(PtH) = 3 Hz. A similar insertion appeared to occur on photolysis of **1** with sulfur. The ^{1}H NMR spectrum of the product mixture contained two clusters of MePt resonances in a 2 : 1 ratio with ^2J(PtH) values of 72 and 63 Hz respectively, corresponding to MePt groups *trans* to bipy and a sulfur donor ligand, respectively, but each of these as well as a MeS cluster at $\delta = 2.2$ ppm contained four individual singlets. Thus it seems that a mixture of complexes [Pt(S_xMe)Me_3(bipy)] is formed. Attempts to separate the mixture were unsuccessful.

The photolysis of [$PtMe_4$(bipy)] with terminal alkynes, RCCH, where R = Me, Ph or CH_2CH_2OH, gave methane and [Pt(CCR)Me_3(bipy)] in high yields. The methane was identified by GC analysis while the alkynylplatinum complexes were identified by their IR and NMR spectra. Each had a resonance in the ^{1}H NMR spectrum with ^2J(PtH) = 51 Hz, due to the MePt group *trans* to acetylide, and each had a strong IR peak at 2100 cm^{-1} due to the alkynyl group.

In contrast to the above reactions, photolysis of **1** with dimethyl acetylenedicarboxylate gave [Pt(O_2CCCCO_2Me)Me_3(bipy)]. The reactivity of methyl esters with **1** was a general one and the reagents RCO_2Me, R = H or Me, each gave [Pt(O_2CR)Me_3(bipy)] on photolysis with **1**. The complexes were identified spectroscopically and were also prepared by the thermal reaction of RCO_2H with **1**. Although each of the photochemical reactions requires loss of two methyl groups, these were not converted quantitatively to either methane or ethane. For example, the reaction with methyl acetate gave 0.34 mol of methane, no detectable ethane and 2.5 mol CO_2. The reaction with MeO_2CCCCO_2Me gave a similar product ratio, whereas methyl formate gave 4.2 mol methane. When the reactions were monitored by ^{1}H NMR, new peaks due to unidentified organic compounds were observed and so it is clear that, although the platinum-containing product is formed cleanly, the organic chemistry is complex.

Quantum yield measurements and a quenching experiment

Quantum yields were measured for several of the above reactions, using incident radiation with $\lambda = 436$ nm. In all solvents except chloroform, the quantum yields were not significantly affected by the presence of oxygen dissolved in the solvents. Data are given in Table 2. It can be seen that the quantum yields are in the range 0.8–1.0, except in the case of photolysis in chloroform which was not degassed. The quantum yield for photolysis in CH_2Cl_2 using incident radiation with $\lambda = 473$ nm was 1.0(1), unchanged from the value of 0.96(3) at $\lambda = 436$ nm. Clearly these are all efficient photochemical reactions and in no case was a significant wavelength dependence of the quantum yield detected. It should be noted that the products of general formula [PtXMe_3(bipy)] are themselves decom-

Table 2

Quantum yields ($\lambda = 436$ nm) for photolysis of [$PtMe_4$(bipy)]

Solvent	Φ (mol einstein^{-1})
CH_2Cl_2	0.96(3)
CH_2Cl_2 [a]	1.0(1)
$CHCl_3$	3.2(2)
$CHCl_3$ [b]	0.83(2)
Me_2CO	0.89(2)
MeOAc	0.81(3)
MeOH	0.81(6)

[a] $\lambda = 473$ nm. [b] Using deoxygenated solvent.

posed by photolysis [7,8], but the quantum yields are much lower and secondary photolysis was negligible under the conditions used in the present work. For example, the quantum yield for photolysis of [$PtIMe_3$(bipy)] is 0.05 at $\lambda = 254$ nm, only 0.01 at $\lambda = 366$ nm [8] and the complex does not absorb at 436 nm.

The photolysis of [$PtMe_4$(bipy)] in CH_2Cl_2 as solvent and reagent was repeated in the presence of the known triplet quencher perylene [Q, E (triplet) = 35.1 kcal mol^{-1}, $\lambda = 814$ nm; E (singlet) = 65.8 kcal mol^{-1}, $\lambda = 435$ nm]. In this experiment the complex was irradiated with incident radiation having $\lambda = 546$ nm in order to preclude absorption by the quencher. Data are given in Table 3. A Stern–Volmer plot of Φ_0/Φ *vs.* $[Q]$, where Φ_0 and Φ are the quantum yields in the absence and presence, respectively, of the quencher Q, gave a straight line with slope of $1.0(1) \times 10^{-2}$ L mol^{-1}. If a diffusion controlled rate of quenching is assumed (k_Q = *ca.* 10^{10} L mol^{-1} s^{-1}), the lifetime of the triplet excited state of [$PtMe_4$(bipy)] can be estimated to be 10^{-8} s. It is likely that all of the photochemical reactions would be similarly quenched and that all occur from the triplet excited state of [$PtMe_4$(bipy)].

CIDNP experiments

Evidence for the intermediacy of free radicals in the photochemical reactions was obtained by the observation of CIDNP effects in the ^1H NMR spectra when photolysis was carried out on solutions in the probe of the NMR spectrometer [5,17–19]. These experiments were also useful for identifying the organic products of the reactions (Fig. 2). Details of the products and their orientations (either enhanced absorption, *A*, or emission, *E*) and ϵ values (– when formed by escape,

Table 3

Effect of the quencher perylene on the quantum yield for photolysis of [$PtMe_4$(bipy)] in CH_2Cl_2

$[Q]/M$	Φ_0/Φ [a]
0	1
8.6×10^{-4}	1.16
5.5×10^{-3}	1.42
1.25×10^{-2}	2.35

[a] Φ_0 is the quantum yield in the absence of quencher; Φ is the quantum yield in the presence of quencher.

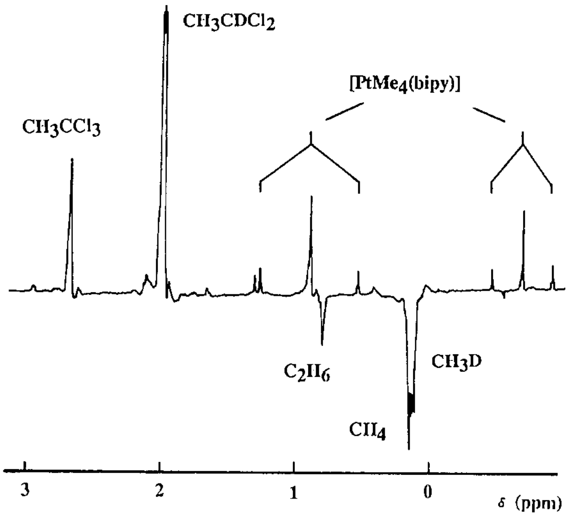


Fig. 2. ^{1}H NMR photo-CIDNP spectrum of [$PtMe_4$(bipy)] in $CDCl_3$.

+ when formed by recombination of the radical pair, assuming the initial radical pair is a triplet as indicated by the quenching experiment) are given in Table 4.

The organic products are generally those expected for reactions involving methyl radicals as intermediates. Photolysis of [$PtMe_4$(bipy)] in CD_2Cl_2 gave both CH_4 and CH_3D among the organic products. The CH_3D is clearly formed from a

Table 4

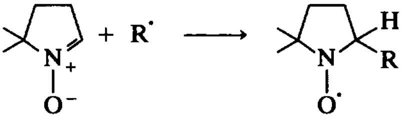
Organic products from photolysis of [$PtMe_4$(bipy)] which give CIDNP effects

Reagent [a] (solvent)	Product	δ (ppm)	Orientation [b]	ε [c]
$CDCl_3$	$\mathrm{C}H_3\mathrm{D}$ [d]	0.12	E	−
	$\mathrm{C}H_3\mathrm{C}H_3$	0.79	E	−
	$\mathrm{C}H_3\mathrm{CDCl_2}$ [e]	2.03	A	+
	$\mathrm{C}H_3\mathrm{CCl_3}$	2.68	A	+
CD_2Cl_2	$\mathrm{C}H_3\mathrm{D}$	0.19	A	+
	$\mathrm{C}H_4$	0.20	A	+
	$\mathrm{C}H_3\mathrm{C}H_3$	0.84	A	+
	$\mathrm{C}H_3\mathrm{CD_2Cl}$	1.44	A	+
	$\mathrm{C}H_3\mathrm{CDCl_2}$	2.04	A	+
CH_2BrCH_2Br	$\mathrm{C}H_4$	0.20	E	−
(CD_3COCD_3)	$\mathrm{C}H_3\mathrm{C}H_3$	0.80	E	−
	$\mathrm{C}H_3\mathrm{CD_2CD(OD)CD_3}$	0.92	A	
	$\mathrm{C}H_3\mathrm{Br}$	2.52	E	−
PhSH	$\mathrm{C}H_3\mathrm{D}$	0.12	A	+
(CD_3COCD_3)	$\mathrm{C}H_4$	0.14	A	+
CD_3OD	$\mathrm{C}H_3\mathrm{D}$	0.19	A	+
	$\mathrm{C}H_4$	0.20	A	+
	$\mathrm{C}H_3\mathrm{C}H_3$	0.87	A	+

[a] Solvent = reagent in some cases. [b] E = enhanced emission, A = enhanced absorption. [c] − = formed by escape, + = formed by recombination with respect to the triplet radical pair. [d] ^2J(HD) gives a 1:1:1 triplet. [e] ^3J(HD) gives a 1:1:1 triplet.

methyl radical abstracting deuterium from the solvent but the CH_4 could be formed by H-abstraction by a methyl radical either from another MePt group or from the bipy ligand. In order to distinguish between these possibilities, the photolysis of [$PtMe_4$(bipy-d_8)] in CD_2Cl_2 was carried out. Only CH_3D was formed and so it is shown that H-abstraction from a MePt group does not occur, and hence that the CH_4 observed on photolysis of [$PtMe_4$(bipy)] in CD_2Cl_2 arises by H-abstraction from the bipy ligand by a methyl radical.

EPR experiments



(1)

Photolysis of either benzene or dichloromethane solutions of [$PtMe_4$(bipy)] in the probe of an EPR spectrometer did not yield an EPR signal, even when frozen solutions were used. However, when the photolyses were carried out in the presence of the radical scavenger dmpo (eq. 1), a strong EPR signal was observed as a 1:1 doublet of 1:1:1 triplets with $a_H = 21.0$ G and $a_N = 14.5$ G. These parameters were identical to those of the radical obtained by photolysis of Me_2Hg in the presence of dmpo. Hence the formation of methyl radicals in the photolysis of [$PtMe_4$(bipy)] is confirmed.

The reaction mechanisms

The reactions with $CDCl_3$ and $BrCH_2CH_2Br$ are most easily interpreted and so will be treated first. On the basis of EPR experiments which indicate that the methyl radical is a primary product of photolysis, the quenching experiment which indicates that reaction occurs from the triplet excited state and the CIDNP experiment in $CDCl_3$ which indicates that the products CH_3D and C_2H_6 are formed by escape from a triplet radical pair while CH_3CDCl_2 and CH_3CCl_3 are formed by recombination, the mechanism of eqs. 2–8 is proposed (~ indicates polarization; where ambiguity exists the simpler mechanism has been chosen).

$$[\mathrm{PtMe_4(bipy)}] \xrightarrow{h\nu} [\mathrm{PtMe_4(bipy)}]^{\mathrm{S}} \longrightarrow [\mathrm{PtMe_4(bipy)}]^{\mathrm{T}} \qquad (2)$$

$$[\mathrm{PtMe_4(bipy)}]^{\mathrm{T}} \longrightarrow \overline{[\mathrm{PtMe_3(bipy)}]^{\cdot} + \mathrm{Me}^{\cdot}}^{\mathrm{T}} \qquad (3)$$

$$\overline{[\mathrm{PtMe_3(bipy)}]^{\cdot} + \mathrm{Me}^{\cdot}}^{\mathrm{T}} + \mathrm{CDCl_3} \longrightarrow \mathrm{CH_3D} + \overline{[\mathrm{PtMe_3(bipy)}]^{\cdot} + \mathrm{CCl_3}^{\cdot}}^{\mathrm{T}} \qquad (4)$$

$$2\tilde{\mathrm{M}}\tilde{\mathrm{e}}^{\cdot} \longrightarrow \mathrm{C_2H_6} \qquad (5)$$

$$\tilde{\mathrm{M}}\tilde{\mathrm{e}}^{\cdot} + \tilde{\mathrm{C}}\tilde{\mathrm{C}}\tilde{\mathrm{l}}_3^{\cdot} \longrightarrow \mathrm{CH_3CCl_3} \qquad (6)$$

$$\overline{[\mathrm{PtMe_3(bipy)}]^{\cdot} + \mathrm{Me}^{\cdot}}^{\mathrm{T}} + \mathrm{CDCl_3} \longrightarrow [\mathrm{PtMe_3Cl(bipy)}] + \overline{\mathrm{CH_3}^{\cdot} + \mathrm{CDCl_2}^{\cdot}}^{\mathrm{T}} \qquad (7)$$

$$\overline{\mathrm{CH_3}^{\cdot} + \mathrm{CDCl_2}^{\cdot}}^{\mathrm{T}} \longrightarrow \mathrm{CH_3CDCl_2} \qquad (8)$$

For the reaction with $C_2H_4Br_2$, the reactions 2 and 3 are followed by eqs. 9–12. Again there is a natural explanation of the CIDNP polarizations for all organic products and the mechanisms are closely related to those proposed for photolysis of other alkyl complexes of gold(I) or platinum(II) [5,18,19].

$$\overline{[\mathrm{PtMe_3(bipy)}]^{\cdot} + \mathrm{Me}^{\cdot}}^{\mathrm{T}} + \mathrm{C_2H_4Br_2} \longrightarrow [\mathrm{PtMe_3Br(bipy)}] + \tilde{\mathrm{M}}\tilde{\mathrm{e}}^{\cdot} + \tilde{\mathrm{C}}_{\tilde{2}}\tilde{\mathrm{H}}_{\tilde{4}}\tilde{\mathrm{B}}\tilde{\mathrm{r}}^{\cdot} \tag{9}$$

$$\tilde{\mathrm{M}}\tilde{\mathrm{e}}^{\cdot} + \mathrm{C_2H_4Br} \longrightarrow \mathrm{CH_4} + \mathrm{C_2H_3Br_2}^{\cdot} \tag{10}$$

$$\tilde{\mathrm{M}}\tilde{\mathrm{e}}^{\cdot} + \mathrm{C_2H_4Br} \longrightarrow \mathrm{CH_3Br} + \mathrm{C_2H_4Br}^{\cdot} \tag{11}$$

$$2\,\tilde{\mathrm{M}}\tilde{\mathrm{e}}^{\cdot} \longrightarrow \mathrm{C_2H_6} \tag{12}$$

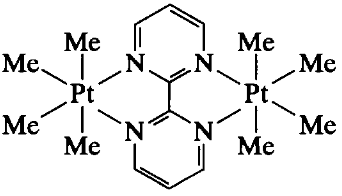
Greater difficulty is found in interpreting the polarizations observed in the photochemical reactions with CD_2Cl_2, CD_3OD and PhSH. In each of these cases, the CH_3D or CH_4 and the C_2H_6 products exhibited enhanced absorption and so, according to Kaptein's rules for a reaction from a triplet radical pair, these products should be formed by recombination within a radical pair [17]. The simplest explanation is that the 17-electron radical $[\mathrm{PtMe_3(bipy)}]^{\cdot}$ is solvated within the primary radical pair and that recombination then occurs by H- or D-abstraction from coordinated solvent by the methyl radical, for example according to eqs. 13 and 14. This might also explain why the methyl radical appears to abstract deuterium from the OD group of CD_3OD rather than the CD_3 group, although the CD bonds are weaker than the OD bond in free CD_3OD. The mechanism requires a shortlived 19-electron intermediate, but this is not a major impediment since such intermediates have been firmly established as reaction intermediates [20].

$$\overline{[\mathrm{PtMe_3(bipy)}]^{\cdot} + \mathrm{Me}^{\cdot}}^{\mathrm{T}} + \mathrm{CD_3OD} \longrightarrow \overline{[\mathrm{PtMe_3(bipy)(CD_3OD)}]^{\cdot} + \mathrm{Me}^{\cdot}}^{\mathrm{T}} \tag{13}$$

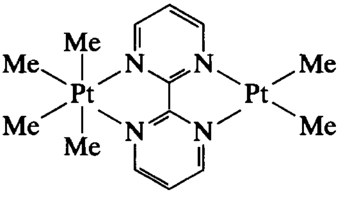
$$\overline{[\mathrm{PtMe_3(bipy)(CD_3OD)}]^{\cdot} + \mathrm{Me}^{\cdot}}^{\mathrm{T}} \longrightarrow \mathrm{CH_3D} + [\mathrm{PtMe_3(OCD_3)(bipy)}] \tag{14}$$

Photochemistry of binuclear platinum complexes

For comparison with the photochemistry of $[\mathrm{PtMe_4(bipy)}]$ described above, a brief study of the binuclear $\mathrm{Pt^{IV}}$–$\mathrm{Pt^{IV}}$ and $\mathrm{Pt^{IV}}$–$\mathrm{Pt^{II}}$ complexes $[\mathrm{Pt_2Me_8(bipym)}]$ (**3**) and $[\mathrm{Pt_2Me_6(bipym)}]$ (**4**), bipym = 2,2′-bipyrimidine [21], was carried out. These complexes absorb at much lower energy than **1**, as illustrated by the data in



(3)



(4)

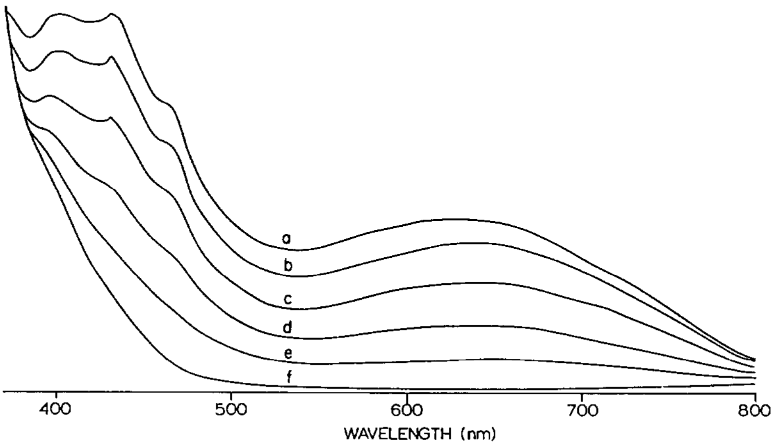


Fig. 3. Electronic spectral changes during the photolysis of [Pt_2Me_8(μ-bipym)] in $CHCl_3$. Total irradiation in minutes: (a) 0; (b) 3; (c) 7; (d) 13; (e) 20; (f) 40. Under similar conditions, photolysis of [$PtMe_4$(bipy)] was complete in 4 min.

Table 1, but the spectra show very similar solvent effects. The blue shift in more polar solvents is typical of MLCT bands. For complex **4**, the lowest energy absorption is probably Pt^{II}, $5d$–π^*(bipym) with the proposed $\sigma[Pt^{IV}–C]–\pi^*$(bipym) band at slightly higher energy, but for complex **3** the lowest energy band must be due to $\sigma[Pt^{IV}–C]–\pi^*$(bipym). Neither complex gave a detectable emission spectrum either at room temperature or at 77 K in ether solution.

Photolysis of complex **3** in chloroform gave [Me_3ClPt(μ-bipym)$PtClMe_3$]. Figure 3 shows the accompanying changes in the visible absorption spectra and the product was easily identified by its NMR spectrum [21]. The reaction is therefore similar to that of [$PtMe_4$(bipy)] with chloroform. In degassed solvent, the quantum yield was 0.14(5), which is considerably lower than the value of 0.83(2) for **1**. This difference can be rationalized in terms of the lower energy of the excited state for **3** (Table 1).

The mixed oxidation state complex [Me_4Pt(μ-bipym)$PtMe_2$] (**4**) was much less photosensitive than either **1** or **3**. Irradiation in CH_2Cl_2 gave very little reaction but a slow reaction did occur in benzene. Extended photolysis gave a black precipitate and a green solution. When the photolysis was monitored by ^1H NMR in C_6D_6, the soluble product was readily identified as [Pt_2Me_8(bipym)] (**3**). It was then suspected that the insoluble black solid might be the known complex [Pt_2Me_4(bipym)] [21], and this was confirmed by comparison of the IR spectrum with that of an authentic sample and by reaction with methyl iodide to give the soluble [Me_3IPt(μ-bipym)$PtIMe_3$], which was identified by NMR [21]. The overall reaction is therefore a disproportionation as shown in eq. 15.

$$2[Me_4Pt(\mu\text{-bipym})PtMe_2] \longrightarrow [Me_4Pt(\mu\text{-bipym})PtMe_4] + [Me_2Pt(\mu\text{-bipym})PtMe_2] \quad (15)$$

The simplest mechanism of reaction 15 would be by transfer of two methyl groups from one molecule to another. To test for this, the photolysis of

$[(CD_3)_4Pt(\mu\text{-bipym})PtMe_2]$ in C_6D_6 was carried out with monitoring by ^1H NMR. The soluble product was $[(CD_3)_4Pt(\mu\text{-bipym})Pt(CD_3)_4]$ and not $[(CD_3)_4Pt(\mu\text{-bipym})PtMe_2(CD_3)_2]$ which would be predicted by this mechanism, and so the mechanism must be rejected. The reaction therefore appears to involve cleavage of Pt(bipym) units followed by recombination. The precipitation of the highly insoluble complex $[Pt_2Me_4(bipym)]$ presumably prevents the reverse reaction from occurring.

Although the mechanism of photolysis of **4** is not completely understood it is significant that no Pt^{IV}–Me bond homolysis occurs, in sharp contrast to the behavior of **1** and **3**. This is presumably because the lowest energy excited state is the triplet Pt^{II}, $5d$–π^*(bipym) state which does not cause reactivity of the Me_4Pt^{IV} center.

Conclusions

Photolysis of $[PtMe_4(bipy)]$ leads to efficient homolysis of a single Me–Pt bond. The evidence is based on EPR, CIDNP and product analysis and, although none of these experiments is either quantitative or unambiguous, the combination provides strong evidence for the homolytic mechanism. Since the 17-electron platinum(III) radical $[PtMe_3(bipy)]^\cdot$ is formed in almost unit quantum yield, its reactivity can be studied. Its most characteristic reaction is halogen abstraction from halocarbons but several other reactions have also been identified. Some evidence for solvation of the radical to give reactive 19-electron radicals $[PtMe_3(S)(bipy)]^\cdot$ has been obtained, where S = CH_2Cl_2, MeOH or PhSH.

It should be noted that 17-electron radicals have previously been suggested as intermediates in free radical oxidative addition reactions to $[PtMe_2(bipy)]$, for example by the propagation reactions of eqs. 16 and 17 [22].

$$^iPr^\cdot + [PtMe_2(bipy)] \longrightarrow [PtMe_2(^iPr)(bipy)]^\cdot \qquad (16)$$

$$[PtMe_2(^iPr)(bipy)]^\cdot + {}^iPrI \longrightarrow [PtIMe_2(^iPr)(bipy) + {}^iPr^\cdot \qquad (17)$$

The rate constant for eq. 16 was calculated to be 10^7 L mol^{-1} s^{-1} and there was no evidence for the reverse reaction. Hence it is not surprising that photolysis of $[PtMe_4(bipy)]$ does not lead to reductive elimination with formation of $[PtMe_2(bipy)]$, as might have been expected by analogy with the known photolysis of $[PtIMe_3(bipy)]$ to give $[PtIMe(bipy)]$ [7,8]. The radical $[PtMe_3(bipy)]^\cdot$ is evidently stable to loss of a methyl radical and the subsequent halogen abstraction with chloroform to give $[PtClMe_3(bipy)]$ is analogous to the known reaction 17 [22]. Clearly radicals $[PtR_3(bipy)]^\cdot$ can be generated as reactive intermediates from either Pt^{II} or Pt^{IV} precursors. There is obviously a strong potential for further applications of such radicals in mechanistic studies and in synthesis.

Experimental

^1H NMR spectra were recorded by using Varian XL100 or XL200 spectrometers. CIDNP measurements were made by using the XL100 spectrometer, with concurrent irradiation using a 200 W Hg/Xe lamp and a quartz light pipe to direct the beam into the sample in the NMR probe. Typically, spectra were collected for

30 s with irradiation, then compared to spectra collected for 30 s without irradiation. Electronic absorption spectra were recorded by using a Cary 118 spectrometer. EPR spectra were recorded by using a Varian E12 spectrometer. Preparative photochemical reactions were carried out using irradiation from a mercury discharge lamp, filtered to remove high energy radiation (< 420 nm). Quantum yields were measured by using a Jasco CRM-FA Spectroirradiator or a PTI Quantacount, calibrated by using ferrioxalate actinometry.

The synthesis of [$PtMe_4$(bipy)], [Pt_2Me_8(μ-bipym)] and [Pt_2Me_6(μ-bipym)] was carried out by the literature methods [10,21].

[$PtMe_4$(bipy)] with $C_2H_4Br_2$

A solution of [$PtMe_4$(bipy)] (50 mg) and $C_2H_4Br_2$ (3 mL) in acetone (12 mL) was irradiated until decolorized (20 min). The solvent was reduced in volume and the product [$PtBrMe_3$(bipy)] (44 mg) was precipitated by addition of pentane (10 mL). It was characterized by comparison of its ^{1}H NMR spectrum with that of an authentic sample [9] and by its MS. Found: $m/z = 475$. $^{195}Pt^{79}BrMe_3$(bipy) calc.: 475; good agreement with calculated isotope pattern.

The synthesis and characterization of [$PtClMe_3$(bipy)] [9], Pt(OMe)Me_3(bipy)] [11], [Pt(SPh)Me_3(bipy)] [11] were carried out in a similar way.

[$PtMe_4$(bipy)] with CS_2

A solution of [$PtMe_4$(bipy)] (50 mg) in freshly distilled CS_2 (500 mL) was irradiated until decolorized. The solvent was evaporated to give the product [Pt(S_2CMe)Me_3(bipy)] as a pale yellow solid, which was purified by crystallization from CH_2Cl_2/pentane. Yield 47 mg. Anal. Found: C, 36.6; H, 4.0; N, 5.5. $C_{15}H_{20}N_2PtS_2$ calc.: C, 36.95; H, 4.1; N, 5.75%. ^{1}H NMR: δ 0.13 (s, 3H, ^2J(PtH) = 59, MePt *trans* to S), 0.91 (s, 6H, ^2J(PtH) = 69.5, MePt *trans* to N), 2.01 (s, ^4J(PtH) = 3, $MeCS_2$).

[$PtMe_4$(bipy)] with MeCCH

A solution of [$PtMe_4$(bipy)] (45 mg) in acetone (10 mL) was saturated with propyne and irradiated until colorless. The solvent was evaporated and the product [Pt(CCMe)Me_3(bipy)] was purified as above. Yield 38 mg. Anal. Found: C, 39.8; H, 4.6; N, 6.2. $C_{16}H_{20}N_2Pt$ calc.: C, 44.1; H, 4.6; N, 6.4%. ^{1}H NMR: δ −0.48 (s, 3H, ^2J(PtH) = 50, MePt *trans* to C), 1.12 (s, 6H, ^2J(PtH) = 73, MePt *trans* to N), 2.70 (s, 3H, MeCC).

Similarly were prepared [Pt($CCCH_2CH_2OH$)Me_3(bipy)] (Anal. Found: C, 43.4; H, 4.6; N, 6.0. $C_{17}H_{22}N_2OPt$ calc.: C, 43.9; H, 4.8; N, 6.0%. ^{1}H NMR: δ −0.38 (s, 3H, ^2J(PtH) = 51, MePt *trans* to C), 1.16 (s, 6H, ^2J(PtH) = 73, MePt *trans* to N), 2.16 [t, 2H, ^3J(HH) = 7, CCH_2), 3.24 (t, 2H, J(HH) = 7, CH_2O). IR: ν(CC) 2100 cm^{-1}.) and [Pt(CCPh)Me_3(bipy)]. Anal. Found: C, 50.9; H, 4.6; N, 5.4. $C_{21}H_{22}N_2Pt$ calc.: C, 50.7; H, 4.5; N, 5.6%. ^{1}H NMR: δ −0.35 (s, 3H, ^2J(PtH) = 51, MePt *trans* to C), 1.20 (s, 6H, ^2J(PtH) = 73, MePt *trans* to N). IR: ν(CC) 2100 cm^{-1}).

[$PtMe_4$(bipy)] with MeOAc

A solution of [$PtMe_4$(bipy)] (50 mg) in MeOAc (20 mL, freshly distilled from K_2CO_3] in a sealed flask was irradiated until decolorized. A sample of the gas phase above the solution was analysed by GC. The solvent was evaporated and the product purified as above and characterized as [Pt(OAc)Me_3(bipy)] by its ^1H NMR spectrum [9].

Similarly were prepared [Pt(O_2CH)Me_3(bipy)] from MeO_2CH (Anal. Found: C, 37.8; H, 4.0; N, 6.5. $C_{14}H_{18}N_2O_2Pt$ calc.: C, 38.1; H, 4.1; N, 6.35%. ^1H NMR: δ 0.44 (s, 3H, ^2J(PtH) = 76, MePt *trans* to O), 1.33 (s, 6H, ^2J(PtH) = 70, MePt *trans* to N).) and [Pt(O_2CCCCO_2Me)Me_3(bipy)] (Anal. Found: C, 41.6; H, 4.0; N, 5.2. $C_{18}H_{20}N_2O_4Pt$ calc.: C, 41.3; H, 3.85; N, 5.35%. ^1H NMR: δ 0.32 (s, 3H, ^2J(PtH) = 77, MePt *trans* to O), 1.20 (s, 6H, ^2J(PtH) = 69, MePt *trans* to N), 3.44 (s, 3H, MeO). IR: ν(CC) 2120 cm^{-1}).

[Pt_2Me_8(bipym)] with $CHCl_3$

A solution of [Pt_2Me_8(bipym)] (20 mg) in $CDCl_3$ (3 mL) was irradiated for 40 min. The ^1H NMR spectrum of the solution showed the formation of a single platinum-containing product [Me_3ClPt(μ-bipym)$PtClMe_3$]. ^1H NMR: δ 0.68 (s, 6H, ^2J(PtH) = 74, MePt *trans* to Cl); 1.52 (s, 12H, ^2J(PtH) = 74, MePt *trans* to N) [21]. This product was isolated and purified as above.

Photolysis of [Me_4Pt(bipym)$PtMe_2$]

A solution of [Pt_2Me_6(bipym)] in C_6D_6 (1.5 mL) was degassed by several freeze-pump-thaw cycles and then flame-sealed in an NMR tube. Irradiation for 1 h led to formation of a green solution and a black precipitate. The soluble complex was identified as [Pt_2Me_8(bipym)] by its NMR spectrum [21]. The black precipitate was isolated and treated with excess MeI to give [$Pt_2I_2Me_6$(bipym)], which was identified by its ^1H NMR spectrum [21].

The complex [$Pt(CD_3)_4Pt$(bipym)$PtMe_2$] was prepared by reaction of [$Pt_2(CD_3)_8(\mu\text{-}SMe_2)_2$] with [$PtMe_2$(bipym)] [21]. Its photolysis was carried out as above.

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