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Preliminary communication

Photochemistry of tetramethyl(2,2′-bipyridine)platinum(IV)

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Abstract

It is shown that photolysis of [$PtMe_4$(bipy)] using incident radiation with λ 436 or 473 nm occurs with high quantum efficiency of 0.8–1.0 to give homolysis of a methyl–platinum bond; this has allowed a study of the chemical reactions of the [$PtMe_3$(bipy)] radical.

It is known that photolysis of transition metal alkyls may occur by homolysis of a metal–carbon bond, but quantum yields are usually low and products are often complex mixtures [1–3]. For example, photolysis of [$PtMe_3(\eta\text{-}C_5H_5)$] using 350 nm incident radiation occurs with a quantum yield of 4.4×10^{-3} and leads to homolysis of a methyl–platinum bond, but the platinum-containing products were complex [4]. For these reasons, mechanistic studies of alkylmetal photochemistry are rare [1–3] (the notable exception being studies of Co–C homolysis in vitamin B_{12} and related model compounds) and relatively little systematic chemistry of the metal radicals, which are produced by homolysis, has been developed. This article describes a mechanistic study of the photolysis of [$PtMe_4$(2,2′-bipyridine)] (**1**) [5,6] which apparently gives the platinum(III) radical [$PtMe_3$(bipy)] in high quantum yield and so allows the chemistry of this very reactive species to be developed. Much of this chemistry is summarized in the Scheme.

The UV-visible spectrum of **1** contains a band in the visible region of the spectrum, which is red shifted in less polar solvents (Table 1) as expected for an MLCT band. We suggest that this band is due to excitation of an electron from a σ(PtC) bond of one of the mutually *trans* methylplatinum groups of **1** to a π^* orbital of bipy and that it leads to efficient homolysis of a Pt–C bond to give a methyl radical and the *fac*-[$PtMe_3$(bipy)] radical. Evidence for methyl radicals was obtained by CIDNP and by spin trapping using dmpo * [6], and the identity of the trapped radical was confirmed by independent formation from Me_2Hg and dmpo; the EPR parameters were identical [7]. The organic products for which CIDNP

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* dmpo = 5,5-dimethylpyrroline *N*-oxide..

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Table 1

The absorption of complex **1** due to the MLCT transition as a function of solvent polarity

Solvent	E_T [a]	λ_{max} (nm) [b]
acetone	42.2	441
pyridine	40.2	449
dichloromethane	41.1	456
tetrahydrofuran	37.4	458
benzene	34.5	475
toluene	33.9	477

[a] Reichardt parameter of solvent polarity. [b] No emission was detected either at room temperature or in ether glass at 77 K. For platinum(IV), the $5d(\mathrm{Pt}) \rightarrow \pi^*(\mathrm{bipy})$ transition is expected at higher energy.

effects were observed are shown in Table 2 note that signals due to methane and ethane could show either enhanced absorption or emission depending on the reagent. The CH_4 formed in the reaction of [$PtMe_4$(bipy)] with CD_2Cl_2 (Table 2) is obtained by methyl radical abstraction of a hydrogen atom from a 2,2′-bipyridine ligand rather than from another methylplatinum group, as shown by the absence of CH_4 on photolysis of [$PtMe_4$(bipy)-d_8)] in CD_2Cl_2.

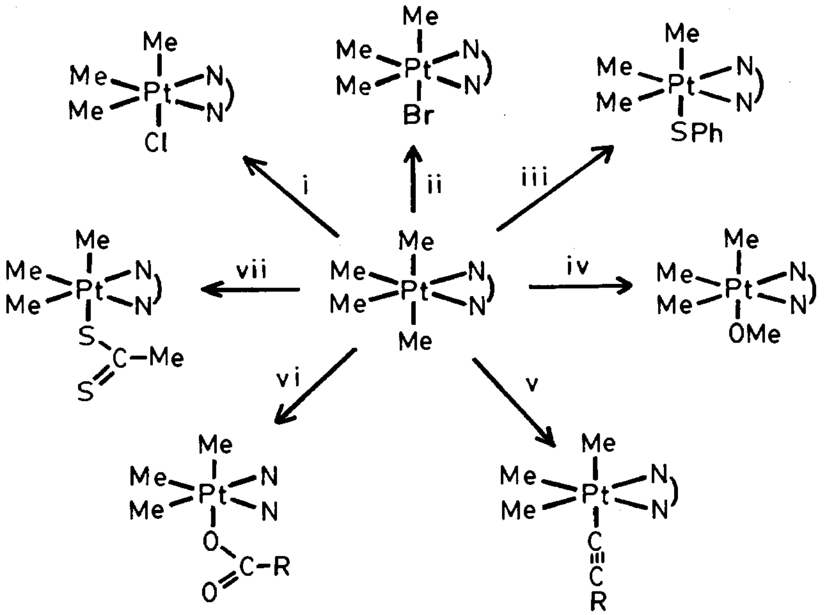
The reaction in CD_2Cl_2 has been studied in greatest detail. The quantum yield for disappearance of [$PtMe_4$(bipy)] was 1.0 ± 0.1 with incident light of wavelength 473 ± 2 nm and 0.96 ± 0.03 at 436 nm. The quantum yields were not significantly affected by the presence or absence of oxygen, but the reaction could be quenched by the triplet quencher perylene, Q, (E_T 35.1 kcal mol^{-1}, λ 814 nm, E_S 65.8 kcal

Table 2

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

Reagent (solvent)	Product	δ (ppm)	Orientation [a]	ϵ [b]
$CDCl_3$	$\mathrm{C}H_3\mathrm{D}$ [c]	0.12	*E*	−
	$\mathrm{C}H_3\mathrm{C}H_3$	0.79	*E*	−
	$\mathrm{C}H_3\mathrm{CDCl_2}$ [d]	2.03	*A*	+
	$\mathrm{C}H_3\mathrm{CCl_3}$	2.68	*A*	+
CD_2Cl_2	$\mathrm{C}H_3\mathrm{D}$ [c]	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 (acetone-d_6)	$\mathrm{C}H_4$	0.20	*E*	−
	$\mathrm{C}H_3\mathrm{C}H_3$	0.80	*E*	−
	$CH_3CD_2CD(OD)CD_3$	0.92	*A*	
	$\mathrm{C}H_3\mathrm{Br}$	2.52	*E*	−
PhSH (acetone-d_6)	$\mathrm{C}H_3\mathrm{D}$ [c]	0.12	*A*	+
	$\mathrm{C}H_4$	0.14	*A*	+
CD_3OD	$\mathrm{C}H_3\mathrm{D}$ [c]	0.19	*A*	+
	$\mathrm{C}H_4$	0.20	*A*	+
	$\mathrm{C}H_3\mathrm{C}H_3$	0.87	*A*	+

[a] *E* = enhanced emission, *A* = enhanced absorption. [b] − = formed by escape, + = formed by recombination of radical pair. These assignments are based on the initial radical pair being a triplet as deduced from the quenching experiment. [c] J(HD) 2 Hz. [d] J(HD) 1 Hz.



Scheme 1. $\widehat{NN}$ = 2,2′-bipyridine. Reagents: $h\nu$ (Hg lamp, filtered to give $\lambda > 420$ nm) and (i) CH_2Cl_2 or $CHCl_3$; (ii) CH_2BrCH_2Br; (iii) PhSH; (iv) MeOH; (v) $RC{\equiv}CH$, R = Me, Ph or CH_2CH_2OH; (vi) RCO_2Me, R = H, Me, CH=CH_2 or $C{\equiv}CCO_2Me$; (vii) CS_2. The solvent was the reagent, acetone or benzene and isolated yields were at least 80%.

mol^{-1}, λ 435 nm). In this experiment, the incident light had λ 546 nm to preclude absorption of light by quencher and to ensure that singlet quenching could not occur. A Stern–Volmer plot of Φ/Φ_Q vs. $[Q]$, where Φ and Φ_Q are the quantum yields in the absence and presence of quencher respectively, gave a straight line of slope 1.0×10^2 l mol^{-1}. If we assume a diffusion controlled rate of quenching ($k_Q \sim 10^{10}$ l mol^{-1} s^{-1}) then the lifetime of the triplet excited state of $[PtMe_4(bipy)]$ in CD_2Cl_2 is estimated to be $\sim 10^{-8}$ s. Similar quantum yields for disappearance of $[PtMe_4(bipy)]$ of 0.83 ± 0.02, 0.89 ± 0.02 and 0.81 were measured for reactions in deoxygenated chloroform, acetone and methanol respectively (λ 436 nm) and we assume that these reactions also occur from the triplet excited state. The quantum yield is ca. 3 for photodecomposition of $[PtMe_4(bipy)]$ in chloroform in the presence of air, and we ascribe this to the known reaction of initially formed $CDCl_2^{\cdot}$ radicals (eq. 1) followed by the thermal reaction of HCl with $[PtMe_4(bipy)]$.

$$CDCl_2^{\cdot} + \tfrac{1}{4}O_2 + \tfrac{1}{2}H_2O \rightarrow CO + 2HCl \qquad (1)$$

The products shown in Scheme 1 are all formed in high yields and were fully characterized. They are almost certainly formed by abstraction or insertion reactions of the radical pair $[PtMe_3(bipy)] \cdot Me^{\cdot}$ formed by the efficient homolysis of a Pt–C bond of $[PtMe_4(bipy)]$. The easy formation of acetylide or carboxylate derivatives from terminal acetylenes or carboxylic esters respectively (Scheme 1) is noteworthy since these appear to be novel photochemical reactions.

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