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Thermal and photochemical addition of alkyl and aryl halides to tetrakis(μ-pyrophosphito)diplatinum(II) tetraanion

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Abstract

Alkyl halides RI (R = Me, Et, n-Pr, i-Pr, n-pentyl, CF_3, CH_2I_2) undergo a thermal reaction with $Pt_2(pop)_4{}^{4-}$ (pop = pyrophosphite) to give the axially substituted "lantern" complexes $Pt_2(pop)_4RI^{4-}$. For R = Me, the pure complex can be isolated. The solution structure has been characterized by a combination of ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy. With the higher homologues, (R = Et, n-Pr, i-Pr, n-pentyl) the reaction gives a mixture of $Pt_2(pop)_4RI^{4-}$ and $Pt_2(pop)_4I_2{}^{4-}$. A radical pathway is proposed. Aryl halides ArX (X = Cl, Ar = Ph; X = Br, Ar = Ph, p-FC_6H_4, p-HOC_6H_4, p-$CH_3OC_6H_4$, p-$HO_2CC_6H_4$, p-$CH_3C_6H_4$; X = I, Ar = Ph) photochemically add to the triplet excited state $Pt_2(pop)_4{}^{4-\star}$ to give $Pt_2(pop)_4ArX^{4-}$. For the photochemical reaction with C_6F_5Br, CCl_4, $CHCl_3$, CH_2ClCO_2H, CH_2BrCO_2H and p-$BrC_6H_4NH_3{}^+$ the product is the dihalo complex $Pt_2(pop)_4X_2{}^{4-}$ (X = Cl, Br).

Introduction

The tetrakis(μ-pyrophosphito)diplatinum(II) tetraanion $Pt_2(pop)_4{}^{4-}$ has the "lantern" type structure with two platinum(II) centers held together in an eclipsed configuration [1]. These non-bonded platinum(II) ions are separated in the complex by 2.925(1) Å, and $Pt_2(pop)_4{}^{4-}$ will add halogens X_2 to give diplatinum(III) complexes $Pt_2(pop)_4X_2{}^{4-}$ [2]. In these product complexes the formation of a bond between platinum(III) centers causes a shortening of the Pt_2 separation into the 2.695(1) Å–2.754(1) Å range [3].

Organometallic diplatium(III) complexes can be prepared in an analogous manner if alkyl or aryl halides (RX) are added to $Pt_2(pop)_4{}^{4-}$ [2,4]. These complexes, like the dihalo adducts, have the R and X substitutents in the axial coordination positions. In this paper we describe the thermal and photochemical reactions which

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can be used to prepare these complexes $Pt_2(pop)_4RX^{4-}$, and we comment briefly on the mechanistic features of these addition reactions.

Experimental

Reagents were purchased as high grade purity, and used without prior purification. The complex $K_4[Pt_2(pop)_4] \cdot 2H_2O$ was synthesized by the literature procedure [5]. Water was distilled from glass prior to use. Enriched (90%) $^{13}CH_3I$ was purchased from MSD Isotopes. Analyses were performed by Canadian Microanalytical Services, Vancouver, B.C., Canada and by Galbraith Laboratories, Knoxville, Tennessee.

Photolyses were carried out in stoppered tubes with solutions purged with nitrogen. The lamp used is a 200 watt mercury lamp in a cooled Ealing housing fitted with a sharp cutoff ($\lambda > 335$ nm) filter. UV-vis spectra were measured on a Hewlett–Packard Model 8451A spectrophotometer with solutions contained in 1 cm path length quartz cuvettes. ^{31}P NMR spectra were measured on an IBM/Bruker AC 200 spectrometer operating at 81.02 MHz. Samples were contained in 10 mm capped tubes using D_2O as internal lock. ^{31}P chemical shifts are referenced (downfield positive) to phosphoric acid. For the complex $Pt_2(pop)_4MeI^{4-}$, the ^1H, ^{31}P and ^{195}Pt NMR spectra were measured on a Nicolet NT 200 spectrometer [6]. Chemial shifts are referenced to tetramethylsilane (^1H and ^{13}C), and external 5.5 *M* H_2PtCl_6 in D_2O (^{195}Pt). Gas chromatographic analyses were carried out using a Hewlett–Packard model 5830A instrument with a 20″ column of 10% UCW.

In the pulsed photolysis experiments, transient species were generated using the 355 nm third harmonic, ca. 10 ns, pulses from a Quantel YG 481 Nd: YAG laser, and were monitored with a conventional xenon lamp, monochromator, photomultiplier arrangement. Digitized signals were passed to a PDP 11/70 computer for analysis. The system has been described more fully elsewhere [7].

The relative quantities of $Pt_2(pop)_4MeI^{4-}$ and $Pt_2(pop)_4I_2^{4-}$ formed in the reaction between $Pt_2(pop)_4^{4-}$ and methyl iodide are calculated from both the absorbance values at 347 and 435 nm and the extinction coefficients for the two compounds at these wavelengths. For $Pt_2(pop)_4MeI^{4-}$, $\epsilon_{347} = 30100$; and for $Pt_2(pop)_4I_2^{4-}$, $\epsilon_{435} = 17400$. In addition, we find that for aqueous solutions of $Pt_2(pop)_4MeI^{4-}$ the ratio of the absorbance intensities at 347 and 435 nm is 25.6/1, and for $Pt_2(pop)_4I_2^{4-}$ (λ_{max} 338 nm) the absorbance ratio of 338 and 347 nm is 1.5/1. The concentration of $Pt_2(pop)_4MeI^{4-}$ is calculated from $A_{347}/30100$ after subtraction of the absorbance due to $Pt_2(pop)_4MeI_2^{4-}$, and the concentration of $Pt_2(pop)_4I_2^{4-}$ is calculated from $A_{435}/17400$, after subtraction of the absorbance at 435 nm due to $Pt_2(pop)_4MeI^{4-}$. In theory this method of analysis requires an iteration, but reasonable accuracy (~ 4%) can be obtained in the $Pt_2(pop)_4MeI^{4-}$ concentration by assuming that all the 435 nm band is due to $Pt_2(pop)_4I_2^{4-}$. No unreacted $Pt_2(pop)_4^{4-}$ is present in the solution as evidenced by ^{31}P NMR spectroscopy. For the higher homologues $Pt_2(pop)_4RI^{4-}$, where we cannot get an absorption spectrum of the pure complex, we can approximate by taking $Pt_2(pop)_4RI^{4-}/Pt_2(pop)_4I_2^{4-}$ as being A_{347}/A_{338}, and by assuming that the relative optical densities are ϵ_{347} $(Pt_2(pop)_4RI^{4-}) = 0.75$ ϵ_{338} $(Pt_2(pop)_4I_2^{4-}$. In the view of the large degree of uncertainty in this method when applied to the higher homologues, we have also analyzed the solutions by $^{31}P\{^1H\}$ NMR spectroscopy.

This latter method has also allowed a second estimate to be made of the relative amounts of $Pt_2(pop)_4^{4-}$, $Pt_2(pop)_4RI^{4-}$ and $Pt_2(pop)_4I_2^{4-}$ present in the solution. The reported values are an average of the two methods.

Tetrapotassium iodomethyltetrakis(μ-pyrophosphito)diplatinum(III): $K_4[Pt_2(pop)_4MeI]$. Methyl iodide (0.2 ml, 3.2 mmol) was added slowly to a stirred solution of $K_4[Pt_2(pop)_4] \cdot 2H_2O$ (0.5 g, 1.2 mmol) in deoxygenated water (ca. 5 ml). The solution changed color from yellow to orange over a period of 30 min. After an additional 30 min, the solution volume was reduced on a rotary evaporator. Cooling to 0 °C and adding ethyl alcohol gave the product as an orange powder. The complex was filtered, washed with ethyl alcohol, and dried in vacuo at ambient temperature. Anal. Found: C, 1.20; H, 0.78; I, 10.4; P, 19.4. $CH_{11}IK_4O_{20}P_8Pt_2$ calcd.: C, 0.95; H, 0.88; I, 10.4; P, 19.6%.

Tetralead bromoaryltetrakis(μ-pyrophosphito)diplatinum(III): $Pb_4[Pt_2(pop\text{-}H)_4ArBr] \cdot 4H_2O$. Aryl bromide (~ 0.1 ml) was added to a solution of $K_4[Pt_2(pop)_4] \cdot 2H_2O$ in deoxygenated water (~ 2 ml) in a Pyrex tube. The solution was photolyzed while the tube was air cooled. After 3 h the aqueous layer was separated, and an aqueous solution of $Pb(OAc)_2$ slowly added. A brown precipitate immediately formed. This precipitate was centrifuged, washed sequentially with water, ethyl alcohol, and diethyl ether, and dried in vacuo at ambient temperature. Anal. ($Ar = C_6H_5$), Found: C, 2.82; H, 0.69. $C_6H_{17}BrP_8O_{24}Pb_4Pt_2$ calcd.; C, 3.6; H, 0.8%. ($Ar = p\text{-}FC_6H_4$), Found: C, 3.03, H, 0.80. $C_6H_{16}BrFP_8O_{24}Pb_4Pt_2$ calcd.: C, 3.5; H, 0.8%. ($Ar = p\text{-}MeOC_6H_4$), Found: C, 2.77; H, 0.70. $C_7H_{17}BrP_8O_{25}Pb_4Pt_2$ calcd.; C, 4.1; H, 0.8%.

Results and discussion

Thermal reactions: When alkyl iodides (RI) are added to aqueous solutions of $Pt_2(pop)_4^{4-}$, the diplatinum(III) complexes $Pt_2(pop)_4RI^{4-}$ (R = Me, Et, n-Pr, i-Pr, n-pentyl) are formed (eq. 1) [3]. The complex $K_4[Pt_2(pop)_4MeI]$ has been isolated in a pure state from this reaction, but for the higher alkyl homologs the complexes have been characterized in solution by a combination of UV-vis and ^{31}P NMR spectroscopy.

$$Pt_2(pop)_4^{4-} + RI \rightarrow Pt_2(pop)_4RI^{4-} \quad (1)$$

The complexes $Pt_2(pop)_4RX^{4-}$ can be identified in the electronic spectrum by the presence of an intense ($\epsilon \approx 4 \times 10^4\ M^{-1}\ cm^{-1}$) absorption in the 320–370 nm range. This absorption has not been definitively assigned, but it is probable that the transition contains components from a $d\sigma^* \leftarrow d\sigma$ and a LMCT ($Pt^{III} \leftarrow X$ or $Pt^{III} \leftarrow R$) transition [8]. The ^{31}P NMR spectra of these complexes show two groups of resonances in the δ 30–40 ppm range for the chemically inequivalent sets of phosphorus nuclei. Each of these multiplets is then coupled to platinum (^{195}Pt, $I = 1/2$, 33.7% abundance), with $^1J(PtP)$ being in the 2000–2500 Hz range. These chemical shift and coupling constant ranges correspond with those found for the axially substituted dihaloplatinum(III) complexes $Pt_2(pop)_4X_2^{4-}$ [2], and differ markedly from the values of δ 66.5 ppm and $^1J(PtP)$ 3075 Hz found for the diplatinum(II) complex $Pt_2(pop)_4^{4-}$ [6].

The single crystal X-ray structure of $K_4[Pt_2(pop)_4MeI]$ confirms that the methyl and iodide ligands are coordinated in the axial positions [9]. The ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectra confirm that this stereochemistry is retained in aqueous solution. The complex is stable in aqueous solution for several days at ambient temperature, and indeed the highest stability of the complex is observed in solutions acidified to a pH in the 1–3 range. This latter observation shows that the designation of the methyl group as a carbanion in the oxidation state formalism does not translate into a corresponding chemical reactivity of the methyl group as a carbanionic base. The ^{1}H NMR spectrum of $Pt_2(pop)_4MeI^{4-}$ in aqueous solution shows an overlapping pattern consisting of 45 lines. The central quintet (δ 1.51 ppm, $^{3}J(PH)$ 5.2 Hz) is flanked by two sets of satellites due to $^{2}J(PtH)$ 52.7 Hz and $^{3}J(PtH)$ 13.8 Hz. Superimposed on these 25 lines are a further 20 lines due to the doubly enriched isotopomer $^{195}Pt_2(pop)_4MeI^{4-}$ (Fig. 1). It should be noted, however, that this assignment is not unambiguous, since we have made the explicit assumption that $^{2}J(PtH) > {}^{3}J(PtH)$. The $^{13}C\{^{1}H\}$ NMR spectrum of the 90% carbon-13 enriched complex $Pt_2(pop)_4{}^{13}CH_3I^{4-}$ shows a center line at δ −2.1 ppm flanked by two sets of satellite doublets due to coupling with ^{195}Pt: $^{1}J(PtC)$ 377 Hz and $^{2}J(PtC)$ 134 Hz. No coupling due to $^{2}J(PC)$ is observed. Additional resonances in the spectrum are due to the approximately 11% contribution from the isotopomer $^{195}Pt_2(pop)_4{}^{13}CH_3I^{4-}$ (Fig. 2). The proton coupled ^{13}C spectrum shows additional quartet multiplicity of each resonance line due to coupling with the hydrogens of the methyl group ($^{1}J(CH)$ 142 Hz). Both the ^{1}H and ^{13}C resonances in this complex are found to be close to the anticipated chemical shift positions, but the value of $^{1}J(PtC)$ is smaller than that for other complexes [10]. This reduced value is likely caused by a high degree of *s*-character in the Pt^{III}–Pt^{III} bond, thereby reducing the *s*-orbital contribution in the Pt–C bond. The $^{31}P\{^{1}H\}$ NMR spectrum shows two quintet

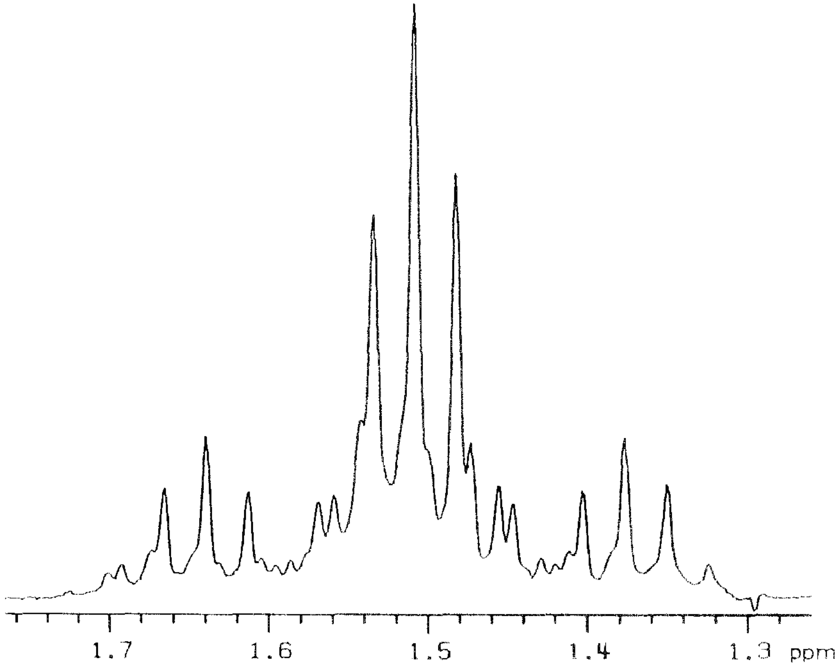

Fig. 1. ^{1}H NMR spectrum of $Pt_2(pop)_4MeI^{4-}$ measured in aqueous solution.

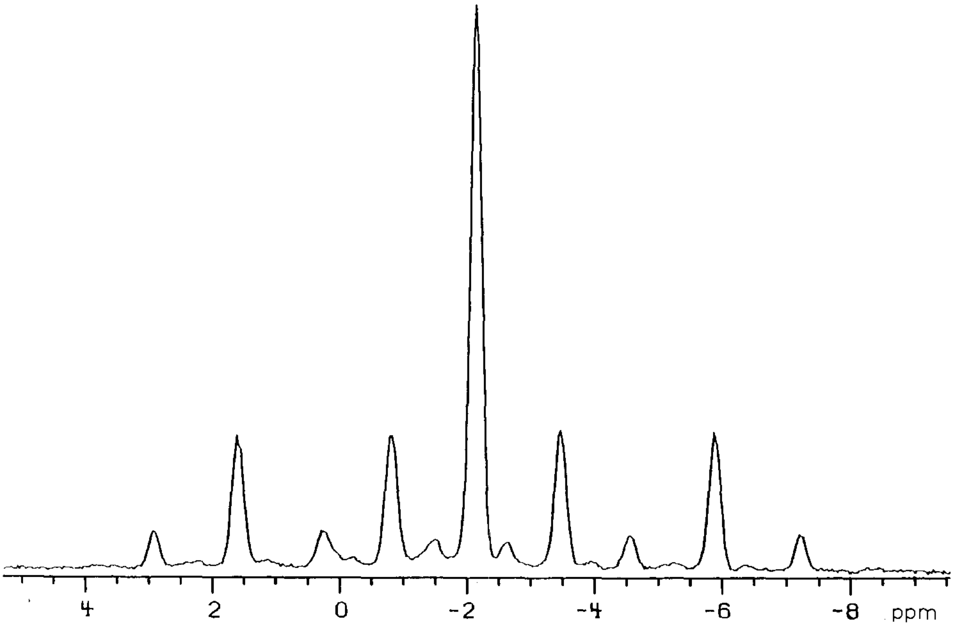

Fig. 2. $^{13}C\{^1H\}$ NMR spectrum of $Pt_2(pop)_4MeI^{4-}$ measured in aqueous solution.

resonances ($^2J(PP) + {}^3J(PP) = 16$ Hz) centered at δ 32.7 and 30.0 ppm, and flanked by satellites due to coupling with ^{195}Pt ($^1J(PtP)$ 2274 and 2454 Hz, respectively). Additional resonances are observed because of the higher order multiplicity of this $[AB]_4XY$ spin system. The ^{195}Pt NMR spectrum shows two quintet of quintets centered at δ -4314 ppm ($^1J(PtP)$ 2274 Hz, $^2J(PtP)$ 46 Hz) and δ -5227 ppm ($^1J(PtP)$ 2454 Hz and $^2J(PtP)$ 86 Hz). By comparison with the complexes $Pt_2(pop)_4I_2{}^{4-}$ (δ(Pt) -5103 ppm), we assign the resonance at δ -5227 ppm in $Pt_2(pop)_4MeI^{4-}$ to the platinum(III) center bonded to iodide. Additional resonances are observed from $^{195}Pt_2(pop)_4MeI^{4-}$ ($^1J(PtPt) \approx 1550$ Hz).

The addition of methyl iodide to $Pt_2(pop)_4{}^{4-}$ is a thermal reaction which is observed even under experimental conditions where light is excluded. Higher homologue alkyl iodides (RI) will also undergo a slow thermal oxidative addition to give "lantern" complexes of the type $Pt_2(pop)_4RI^{4-}$. The reactions proceed more slowly than does that with methyl iodide; even after 4 days the addition is incomplete. A second difference from the methyl iodide reaction is that the solution formed at the completion of the reaction always contains significant amounts of $Pt_2(pop)_4I_2{}^{4-}$ (eq. 2). We find no evidence for the formation of $Pt_2(pop)_4R_2{}^{4-}$.

$$Pt_2(pop)_4{}^{4-} \xrightarrow{RI} \begin{cases} \rightarrow Pt_2(pop)_4RI^{4-} \\ \rightarrow Pt_2(pop)_4I_2{}^{4-} \end{cases} \qquad (2)$$

The formation of the alkyl complexes $Pt_2(pop)_4RI^{4-}$ has been confirmed by a combination of UV-vis and ^{31}P NMR spectroscopy (Table 1), and by isolation of the impure compound as the Pb^{2+} salts. The simultaneous formation of $Pt_2(pop)_4RI^{4-}$ and $Pt_2(pop)_4I_2{}^{4-}$ is suggestive of an addition reaction which

Table 1

Spectroscopic data on the diplatinum(III) complexes $Pt_2(pop)_4RX^{4-}$ [a]

Complex		λ_{max} (nm)	$\delta(^{31}P)$ (ppm) ($^1J(PtP)$ (Hz))	
R	X			
CH_3	I	347	30.3 (2454).	32.7 (2274)
C_2H_5	I	352	33.4 (2465),	35.2 (2339)
n-C_3H_7	I	358	34.3 (2405).	36.3 (2216)
i-C_3H_7I	I [b]	358	32.6	32.2
CF_3	I	324	25.0 (2200),	26.0 (2362)
CH_2I	I	334, 372	29.8 (2382),	31.5 (2260)
n-C_5H_{11}	I	358	31.6 (2446),	33.5 (2252)
C_6H_5	I	360	30.5 (2428),	31.6 (2236)
C_6H_5	Br	326	32.6 (2284),	37.0 (2474)
p-FC_6H_4	Br	326	31.9 (2233),	36.2 (2432)
p-HOC_6H_4	Br	321	32.3 (2254),	36.8 (2468)
p-$CH_3OC_6H_4$	Br	327	32.1 (2222),	36.7 (2441)
p-$HO_2CC_6H_4$	Br [c]	326	32.0 (2226),	34.1 (2390)
p-$CH_3C_6H_4$	Br [c]	326	32.1 (2220),	34.1 (2400)
C_6H_5	Cl [c]	328	35.8 (2188),	36.6 (2458)

[a] Data measured in aqueous solution. [b] Platinum-195 satellites not assigned. [c] Spectra measured in aqueous DMSO solution.

occurs by a radical pathway [11]. A number of experiments have been carried out to probe the mechanism of this thermal addition reaction. These data for methyl iodide are collected in Table 2. The added reagents have been chosen because earlier studies on the addition of alkyl halides to $Co(CN)_5^{3-}$ have shown that they react to trap free alkyl radicals [12]. Of these added compounds, several cause the formation of small but measurable quantities of $Pt_2(pop)_4I_2^{4-}$. Among these are α-methylstyrene and oxygen. In the presence of α-methylstyrene we find that approximately 10% of $Pt_2(pop)_4I_2^{4-}$ is formed. When oxygen is used as a potential radical trap, a significant loss of selectivity to $Pt_2(pop)_4RI^{4-}$ is also observed. However, in this case the estimation of the relative contribution from each reaction pathway to give $Pt_2(pop)_4MeI$ and $Pt_2(pop)_4I_2^{4-}$ is difficult to estimate because of the possible

Table 2

Distribution of products from trapping reagents in the thermal reaction (24 h [a]) between $Pt_2(pop)_4^{4-}$ and MeI (R = Me) [b]

Trap	Fraction ($Pt_2(pop)_4I_2^{4-}$
None	0.00
Hydroquinone	0.01
Acrylonitrile	0.07
Methyl acrylate	0.07
α-Methylstyrene	0.10
Oxygen (1 atm)	0.26
Oxygen (130 atm)	0.36
Ascorbic acid	0.00
Isopropyl alcohol	0.07

[a] After this time the reaction is complete. [b] The solvent is water or a 1/1 mixture of water and methanol. The reaction occurs in the aqueous methanolic phase.

formation of small quantities of iodine in the oxidation of methyl iodide by oxygen, and its subsequent rapid addition to $Pt_2(pop)_4^{4-}$ to give $Pt_2(pop)_4I_2^{4-}$ [13*]. For the case of methyl iodide addition we cannot exclude the possibility that an ionic (S_N2) mechanism is operative, but since radical traps do cause some small decrease in the selectivity, it is more likely that a cage radical pathway occurs where the methyl radical is rapidly trapped by $Pt_2(pop)_4X^{4-}$ [14].

The reactions of $Pt_2(pop)_4^{4-}$ with the higher homologue alkyl iodides RI (R = Et, n-Pr, i-Pr, n-pentyl) give much higher amounts of the iodo complex in the solution after some 4–6 days reaction time. Analyses by UV-vis spectroscopy (rough estimates from A_{347}/A_{331} with the assumption that $\epsilon(Pt_2(pop)_4RI^{4-}) = 0.75\ \epsilon(Pt_2(pop)_4I_2^{4-})$ as was found for the methyl complex), or by $^{31}P\{^1H\}$ NMR spectroscopy, show that the percentage of $Pt_2(pop)_4I_2^{4-}$ in the reaction mixture is approximately 40–60% of the total product. After 4–6 days we still find unreacted $Pt_2(pop)_4^{4-}$ present in the solution. Each alkyl analog produces a similar percentage of $Pt_2(pop)_4I_2^{4-}$. For R = Et, n-Pr and i-Pr we have also carried out the reaction in a mixed solvent (water/methanol 1/1) with added acrylonitrile or α-methylstyrene, and we find no major change in the ratio of $Pt_2(pop)_4RI^{4-}$ to $Pt_2(pop)_4I_2^{4-}$ formed in the reaction, although small changes of up to 10% are not detected. No unambiguous mechanistic details are revealed from these trapping reactions, but a higher proportion of $Pt_2(pop)_4I_2^{4-}$ is to be expected in the product if these higher homologue radicals ($R^\cdot$) react more slowly with $Pt_2(pop)_4I^{4-}$ formed by halogen atom abstraction from RI (eq. 3) than does a second molecule of RI. If this radical pathway is operative we must postulate that the olefin trapping agents do not react

$$Pt_2(pop)_4^{4-} + RI \rightarrow Pt_2(pop)_4I^{4-} + R^\cdot \qquad (3)$$

sufficiently rapidly with the alkyl radicals to cause $Pt_2(pop)_4I_2^{4-}$ to become the sole product.

Some support for the formation of $Pt_2(pop)_4I^{4-}$ as an intermediate is found in the observation that no reaction occurs between $Pt_2(pop)_4^{4-}$ and RI (R = n-Pr, i-Pr, n-pentyl) in the presence of a large excess of ascorbic acid. Since the complexes $Pt_2(pop)_4RI^{4-}$ and $Pt_2(pop)_4I_2^{4-}$ are not reduced by ascorbic acid under the experimental conditions of these reactions, a viable explanation is that the mixed valence intermediate $Pt_2(pop)_4I^{4-}$ is rapidly reduced back to $Pt_2(pop)_4^{4-}$ by ascorbic acid before it reacts to give diplatinum(III) products.

Photochemical reactions. Aryl halides (ArX) do not add to $Pt_2(pop)_4^{4-}$ under thermal conditions. Photochemically, however, oxidative addition occurs to give the haloaryldiplatinum(III) complexes $Pt_2(pop)_4ArX^{4-}$ where the aryl and halide ligand are coordinated in the axial positions (eq. 4). The reactive intermediate is the triplet excited state $Pt_2(pop)_4^{4-*}$, which can be confirmed by the observation that no reaction is observed in the presence of the triplet state quenchers sulfur dioxide or hydroquinone [15]. The quenching of $Pt_2(pop)_4^{4-\star}$ is apparent from the color change of the photolyzed solution from luminescent green to yellow. The complexes $Pt_2(pop)_4ArX^{4-}$ are not reduced by sulfur dioxide or hydroquinone. The range of

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* This and other references marked with asterisks indicate notes occurring in the list of references.

aryl halides used is shown in Table 1. The complexes $Pt_2(pop)_4ArX^{4-}$ show ab-

$$Pt_2(pop)_4^{4-\star} + ArX \rightarrow Pt_2(pop)_4ArX^{4-} \qquad (4)$$

sorption bands in the 320–330 nm range, and two sets of resonances in the ^{31}P NMR spectrum between δ 30 and 40 ppm. The reduced coupling to ^{195}Pt ($^1J(PtP) \approx$ 2300 Hz) confirms that oxidative addition to give platinum(III) centers has occurred in reaction 4.

Using transient difference spectroscopy, we have found that the first step in this photoreaction involves bromine atom abstraction from aryl bromides by the triplet excited state $Pt_2(pop)_4^{4-\star}$ (eq. 5) [16]. The mixed valence diplatinum(II,III) inter-

$$Pt_2(pop)_4^{4-\star} + ArBr \rightarrow Pt_2(pop)_4Br^{4-} + Ar^{\cdot} \qquad (5)$$

mediate $Pt_2(pop)_4Br^{4-}$ is characterized by a transient absorption band at 340 nm (Fig. 3). This transient absorption band grows in very rapidly after the pulse with a $t_{1/2} < 100$ ns. This bromine abstraction reaction from aryl halides is too fast for the addition to occur by an electron transfer $S_{RN}1$ pathway. This claim is particularly applicable to an aryl halide such as C_6F_5Br. Savéant has shown that the rate of loss of halide ion from the aryl halide radical anion is dependent on the electrode potential of the aryl halide, and from these data we can calculate that the rate constant for the loss of bromide ion from $C_6F_5Br^-$ will be in the region of 10^{-2} s^{-1} [17]. This rate is slower than the overall rate of formation of $Pt_2(pop)_4Br^{4-}$ by a factor of some 10^8; therefore a multistep $S_{RN}1$ pathway to give $Pt_2(pop)_4Br^{4-}$ is unfeasible. For the cases of Ar being C_6H_5, p-FC_6H_4, p-HOC_6H_4, p-$CH_3OC_6H_4$, p-$HO_2CC_6H_4$, p-$CH_3C_6H_4$ the product $Pt_2(pop)_4ArBr^{4-}$ appears to be formed with high selectivity in the early stages of the photochemical reaction, but as photolysis continues, increasing amounts of $Pt_2(pop)_4Br_2^{4-}$ (λ_{max} 305 nm) are obtained. The formation of $Pt_2(pop)_4ArBr^{4-}$ from $Pt_2(pop)_4Br^{4-}$ is explicable if there is a rapid recombination between $Pt_2(pop)_4Br^{4-}$ and $Ar^{\cdot}$ to give the final product $Pt_2(pop)_4ArBr^{4-}$ (eq. 6). The progressive formation of $Pt_2(pop)_4Br_2^{4-}$ under prolonged photolysis is to be expected if reaction 6 is photochemically reversible, with $Pt_2(pop)_4Br^{4-}$ being trapped by halogen abstraction from ArBr (eq. 7). In support of this pathway shown in eq. 7, we find that with bromobenzene and bromopentafluorobenzene the radical coupling products biphenyl and decafluorobiphenyl are detected as by-products of the photochemical reaction. These compounds have been detected using glc by comparing with authentic commercial

$$Pt_2(pop)_4Br^{4-} + Ar^{\cdot} \rightarrow Pt_2(pop)_4ArBr^{4-} \qquad (6)$$

$$Pt_2(pop)_4ArBr^{4-} + ArBr \xrightarrow{h\nu} Pt_2(pop)_4Br_2^{4-} + Ar_2 \qquad (7)$$

samples. The impure aryl halide adducts can be isolated as their Pb^{2+} salts by addition of aqueous solutions of lead acetate to solutions of the complex. The analytical data are rather unsatisfactory because of contamination of the product with the dibromo adduct. In some cases, however, this photochemical pathway to give $Pt_2(pop)_4ArX^{4-}$ is not followed, and the final product is the dihalo complex $Pt_2(pop)_4X_2^{4-}$. This situation is found in the photochemical reaction between $Pt_2(pop)_4^{4-}$ and C_6F_5Br, CCl_4, $CHCl_3$, CH_2ClCO_2H, CH_2BrCO_2H, p-$BrC_6H_4NH_3^+$. We conclude in this case that the reactions between $R^{\cdot}$ and $Pt_2(pop)_4^{4-}$ or

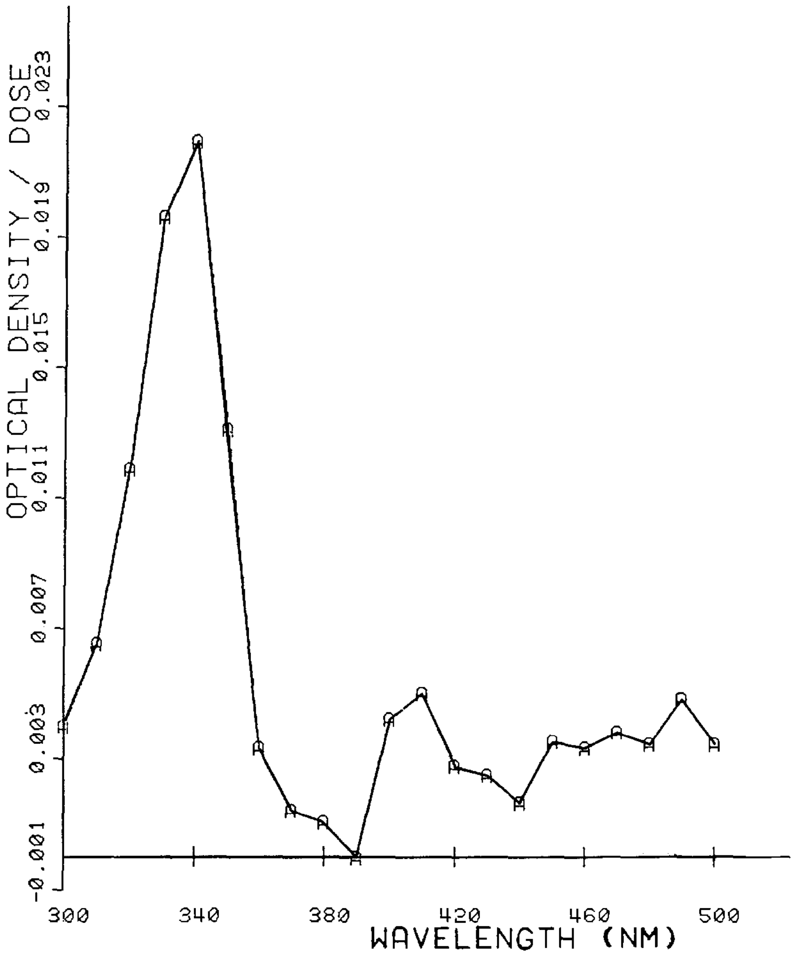

Fig. 3. Transient difference spectrum of $Pt_2(pop)_4Br^{4-}$ formed by the reaction between $Pt_2(pop)_4^{4-*}$ and C_6H_5Br. The spectrum was measured 0.1 μs after the laser pulse.

$Pt_2(pop)_4X^{4-}$ do not occur to any significant extent before the dihalo product is formed by the halogen atom abstraction reaction of $Pt(pop)_4X^{4-}$ with RX.

Acknowledgment

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