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Unexpected, Photochemically Induced Activation of the Tetrabutylammonium Cation by Hexachloroplatinate(IV)

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A dinuclear, butadiene-bridged complex, *trans*- μ^2 : η^2 , η^2 -1,3-butadiene-bis(trichloroplatinate(II)) (1) was unexpectedly obtained on photolysis of acetone solutions of $(\text{NBu}_4)_2[\text{PtCl}_6]$.

There is some interest in realising water-soluble, heterobimetallic complexes that could be used as a source of two different metals for the preparation of mesoporous silicas with well-defined, heterobimetallic nanoparticles. Thus, following on from our methodology of using Ru surfactants to realise RuO₂-doped mesoporous silicas,¹ we developed a more general approach that used ethylene oxide surfactants to form the mesophase in water into which had been dissolved metal salts with alkali metal cations.^{2,3} The approach was successful using both inert halometallate complexes of right-hand-side transition elements of the second and third rows as well as anionic EDTA complexes of a range of metals. Mixed-metal nanoparticles containing Pt and Co could be realised by using a mixture of K₂[PtCl₄] and Na[Co(EDTA)],³ but their constitution varied widely and it was for this reason that well-defined bimetallic precursors were sought. Use of TTHA (triethylenetetramine-*N,N,N',N'',N''',N''''*-hexaacetic acid – homologated EDTA) gave limited success,⁴ but it did prove possible to obtain [Cl₂Pd(μ -Cl)₂PtCl₂]²⁻ by reaction of [PtCl₄]²⁻ and [PdCl₄]²⁻ as their [K(18-crown-6)]⁺ salts. The solid obtained was shown to contain [Cl₂Pd(μ -Cl)₂PdCl₂]²⁻, [Cl₂Pt(μ -Cl)₂PtCl₂]²⁻ and [Cl₂Pd(μ -Cl)₂PtCl₂]²⁻, the heterobinuclear target being obtained as about 25% of an inseparable mixture.⁵

Curious to see if this latter approach could be applied more generally and also if a pure, heterobimetallic product could be obtained, reactions were carried out between [PtCl₄]²⁻ and [AuCl₄]⁻ in aqueous solution as potassium salts. In all cases,

there was an instantaneous oxidation of the Pt^{II} to Pt^{IV} with concomitant reduction of Au^{III} to Au^I or Au⁰ depending on the stoichiometry. For example, reaction of an aqueous 3 : 2 mixture of [PtCl₄]²⁻ and [AuCl₄]⁻ led to the formation of a gold mirror after which the mixture was filtered to leave a solution that was then treated with Bu₄NCl in order to precipitate anionic species remaining in solution. On one occasion, single crystals formed from such a solution that had been left to crystallise and were subject to analysis by X-ray diffraction. Remarkably, the structure (Fig. 1) revealed a dinuclear complex of Pt^{II} (1) in which *trans*-1,3-butadiene is coordinated at each double bond by a trichloroplatinate(II) fragment with two Bu₄N⁺ as counter cation.

This complex was first reported in 1957 by Slade and Jonassen as its potassium salt,⁶ being prepared by bubbling butadiene through an acidic solution of K₂[PtCl₄]. In common with [Fe(CO)₃(η^4 -butadiene)], it was found to be remarkably stable thermally, not showing signs of decomposition below 240 °C under the conditions reported.⁶ The structure was given as having a butadiene unit bridging two PtCl₃ units on the basis of infrared evidence, but the detail showing the actual geometry was only elucidated in 1967 through a detailed infrared study by Grogan and Nakamoto.⁷ The X-ray single crystal structure was then determined by Adam *et al.* as the NMe₂Et⁺ salt, although rather few details were given.⁸

The present determination (*R*₁ = 3.60%) gives a C=C distance of 1.403(7) Å and a C–C separation of 1.453(7) Å (compare 1.36(3) and 1.51(3) reported in ref. 8). The distances are statistically different, although it is interesting to note the much

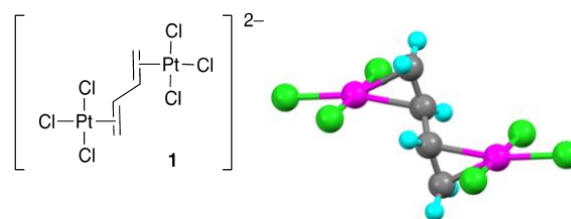


Figure 1 Molecular structure of the [Cl₃Pt(μ^2 : η^2 -1,3-butadiene)PtCl₃]²⁻ dianion.

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greater elongation of the C=C double bond (1.337(2) Å)⁹ compared to Zeise's salt (1.375(4) Å);¹⁰ indeed the C=C bond length is close to those found in [Fe(CO)₃(*η*⁴-butadiene)] (*ca* 1.4196 Å).¹¹ Interestingly, in Zeise's salt,¹⁰ the Pt–Cl bond length *trans* to ethene is 2.3397 Å compared to 2.30 Å for the other Pt–Cl distances (and in [PtCl₄]²⁻),¹² suggesting a significant *trans*-influence, whereas in **1**, the Pt–Cl bond length *trans* to the alkene is unchanged at 2.302(1) Å. The reason for these differences is not apparent, although it is noteworthy that while in Zeise's salt the alkene C=C bond is effectively perpendicular to the PtCl₃ plane (angle = 1.047(12)°), in **1** it makes an angle of 9.1(3)° (Fig. 2).

Formation of **1** was unexpected and so the reaction was investigated further to understand the observed reactivity. The presence of butadiene in the product suggested involvement of Bu₄N⁺ and so initial reactions were conducted in acetone stirring the Bu₄N⁺ salts of [AuCl₄]⁻ and [PtCl₄]²⁺ together. Given that in acetone, too, the oxidation of the platinum(II) appeared both rapid and complete, it was reasoned that the gold(III) served only to oxidise the platinum and so the reaction was carried out by stirring pre-prepared [Bu₄N]₂[PtCl₆] alone in acetone. This also led to product formation and the reaction rate was improved by heating under reflux. That the Bu₄N⁺ cation was the source of the butadiene was demonstrated clearly by repeating the reaction successfully in CH₂Cl₂.

In order for the product to form, there needs to be an extrusion of a butyl group from the ammonium cation, a reduction of the platinum and, with the degree of unsaturation present in the product ligand, C–H activation. [PtCl₆]²⁻ is evidently the active agent, but it is not known to react thermally unless in the presence of acid.¹³ However, there are reports of photochemical C–H bond activation mediated by [PtCl₆]²⁻,¹⁴ and control experiments then showed that formation of **1** did not proceed in the dark, rather occurring smoothly under UV irradiation (medium-pressure Hg discharge lamp) at room temperature in both acetone and CH₂Cl₂.¹⁵ Thus, the success of reactions so far studied had resulted from the mediation of ambient light. The product of these reactions was isolated by removing the solvent *in vacuo* and then crystallising exhaustively from acetone/diethyl ether. After several such cycles the recovered yield of **1** was up to around 65%, demonstrating that it is the preferred pathway and not simply a side-product of some other reaction. Crystallisation always led to the *anti,trans*-conformer but, as noted in the SI, on dissolution, the *syn,trans*- and *anti,cis*-conformers were also visible by NMR spectroscopy.

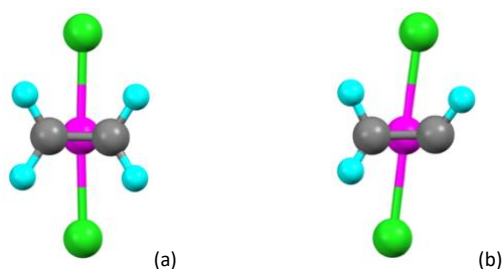


Figure 2. View of the disposition of the PtCl₃ plane with respect to the alkene double bond (a) in Zeise's salt¹⁰ and (b) in complex **1**.

That photolysis of [PtCl₆]²⁻ leads to a Pt^{III} species was suggested as long ago as the 1950s¹⁶ and was confirmed by studies in the early 1970s, mostly concerning photoacquistion.^{17,18} However, the literature of the photoinduced reactivity of [PtCl₆]²⁻ tends to originate in the 1980s from the group of Shul'pin and the proposed mechanism relies on the reduction of a photochemically excited state of [PtCl₆]²⁻ by a reacting organic fragment, leading to a Pt^{III} species such as [Pt^{III}Cl₅]²⁻ which can react further with reduction to Pt^{II}.¹⁹ Given that it was suggested that an excited state of hexachloroplatinate(IV) plays an important role, theoretical investigations of the electronic structure of the excited state of [PtCl₆]²⁻ were conducted using a density functional theory (DFT) approach. Both ground-state geometry optimisation and time-dependent (TDDFT) calculations were performed at the B3LYP/TZVP level of theory¹⁹ utilising ORCA 2.9 code. An effective core potential (ECP) was applied on the platinum ato,^{20,21} and a conductor-like screening model (COSMO) was used to accommodate the electrostatic interaction of molecule with solvent by adding the dielectric constant (*n*_D) and relative permittivity (*ε*) parameters of the solvent into the calculation.²² In this case, the solvent was acetone (*ε* = 20.7 F m⁻¹; *n*_D = 1.359).

The calculated absorption spectrum of [PtCl₆]²⁻ in acetone expressed as oscillator strength versus wavelength showed two main bands at 324 nm and 207 nm (Fig. 3a). The spectrum mirrored the UV spectrum of the complex obtained from the experiment, implying reasonable agreement with the calculation used. According to the TDDFT calculations, the intense band at λ_{max} = 207 nm corresponds to a transition from the ground state (S₀) to an excited singlet state (S₃₁), S₀ → S₃₁. The visualisation of electron density difference between the two states suggests that the S₃₁ state has mixed metal-to-ligand charge-transfer (MLCT) and ligand-to-ligand charge-transfer (LL'CT) character, which together can be denoted as MLL'CT. The absorption band of lower intensity (λ_{max} = 324 nm) is attributed to an S₀ → S₂₂ transition, and the visualisation of electron density difference between S₀ and S₂₂ suggests a mixed character of ligand-to-ligand charge transfer (LL'CT) and ligand-to-metal charge transfer (LMCT), labelled as LML'CT.

Since the compound contains a heavy Pt atom that provides strong spin-orbit coupling and, consequently, fast inter-system-crossing between singlet and triplet states, it was suggested that the excited state, in which the compound reacts, is the lowest excited triplet state (T₁). Its optimised geometry reveals Pt–Cl bond length changes along the z-axis of 0.36 Å from 2.47 Å in the ground state to 2.83 Å in the T₁ state, while the other four Pt–Cl bonds were shortened by 0.19 Å to 2.28 Å. The character of the T₁ state in its equilibrium geometry can be assigned as ligand-to-ligand charge transfer (LL'CT) (Fig. 3b). The bond elongation populates the anti-bonding Pt–Cl σ* orbital, almost certainly leading to cleavage of the z-axis Pt–Cl bonds as shown in Fig. 3b; those two bonds are the same length. This observation is in accordance with aspects of a related experimental and theoretical study reported by Kaufman *et al.*²³

To validate further the results from theory, a solution of [Bu₄N][PtCl₆] in acetone was cooled to 120 K and irradiated in the cavity of an EPR spectrometer. After two minutes of

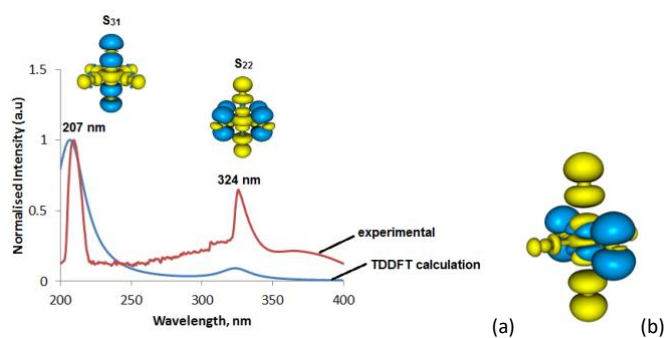


Figure 3 (a) The electronic spectra of $[\text{PtCl}_6]^{2-}$ from the experimental method and the calculation along with the visualisation of electron density difference between the ground state and the excited state associated with the states of S_{31} (207 nm) and S_{22} (324 nm) (note: yellow: increasing of electron density and blue: decreasing of electron density compared to the ground state); (b) electron density difference between the ground state (S_0) and the T_1 state calculated for $[\text{PtCl}_6]^{2-}$ in relaxed T_1 state geometry (note: yellow: increased electron density and blue: decreased electron density compared to the ground state).

irradiation, a spectrum was observed with a signal at $g = 2.402$, whose intensity increased with time so that at 50 mins, a singlet was observed flanked by doublet satellites (Fig. 4a). This was clearly a Pt-based radical with satellites from coupling to ^{195}Pt ($I = \frac{1}{2}$, 33.8%; $a_{\text{Pt}} = 42.5$ mT). From previous work on irradiation of single crystals of $\text{K}_2[\text{PtCl}_4]$, the signal is identified as the Pt^{III} species $[\text{PtCl}_5]^{2-}$,²⁴ consistent with the results of calculation and implying production of Cl^\bullet . These observations are also consistent with those made by Nizova *et al.* on irradiation of $\text{H}_2[\text{PtCl}_6]$ in frozen acetone.¹⁸

In addition, a peak corresponding to an organic radical was observed with $g = 2.0084$ (Fig. 4b) and it is noted that a rather similar spectrum was reported by Eastland *et al.* for the $\text{NET}_3^{+\bullet}$ radical cation (Fig. 4c, which shows only coupling to ^{14}N).²⁵ Thus, it would appear that irradiation of a solid solution of $[\text{Bu}_4\text{N}]_2[\text{PtCl}_6]$ generates Pt^{III} , Cl^\bullet and a nitrogen-based radical.

Formation of butene from Bu_4N^+ is known to occur *via* the Hofmann elimination in which a β -hydrogen is removed as H^+ and the electron pair from the bond move to the nitrogen generating Bu_3N .²⁶ However, there is also a report of a radical-initiated Hofmann elimination from Bu_4N^+ , the hydrogen being abstracted by a photochemically generated benzophenone radical anion.²⁷ Such a radical mechanism is consistent with our observations of the photochemical formation of Pt^{III} accompanied by formation of Cl^\bullet which abstracts H^+ from NBu_4^+ leading ultimately to butene, which could generate an intermediate complex $[\text{PtCl}_3(1\text{-butene})]^-$.¹⁸

A realistic pathway for formation of butadiene then requires a second C–H activation, which we propose is also mediated photochemically using a second equivalent of $[\text{PtCl}_6]^{2-}$, which is entirely consistent with the work of Shul'pin *et al.* who showed how irradiation of solutions of $[\text{PtCl}_6]^{2-}$ -containing hexane led to the formation of $[\text{PtCl}_2(\eta^2\text{-1-hexene})(\text{py})]$ (isolated by trapping with pyridine).²⁸ The $[\text{Pt}^{\text{III}}\text{Cl}_5]^{2-}$ anion was again implicated in the reaction.

Mechanistically, the question then arises as to the order of reactions. A first step could activate a butyl group of NBu_4^+ to yield PtCl_3^- bound η^2 to $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}_2-\text{NBu}_3^+$, which then

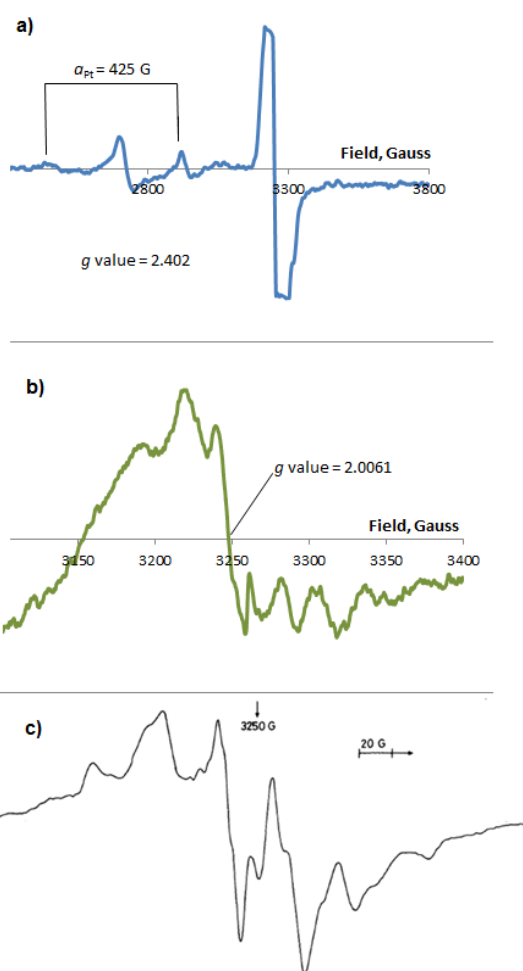


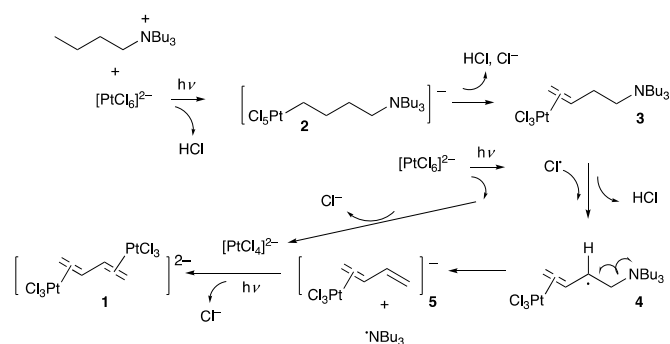
Figure 4: The EPR spectrum of $[\text{Bu}_4\text{N}]_2[\text{PtCl}_6]$ on irradiation for 20 minutes in dichloromethane at 120 K. a) on wide range, b) enlargement in the organic area and c) $\text{Et}_3\text{N}^{\bullet+}$ as reported in ref. 25.

undergoes a Hofmann elimination to give the butadiene product. Alternatively, The Hofmann pathway could go first to form $[\text{PtCl}_3(1\text{-butene})]^-$ which is activated in a second step to give the product.

In order to see if it was possible to determine a sequence of reactivity, an experiment was carried out in which $[\text{PPN}][\text{PtCl}_3(1\text{-butene})]^{29}$ and $[\text{PPN}]_2[\text{PtCl}_6]$ were dissolved in acetone and irradiated under the same conditions as the other photolyses; no formation of **1** was observed. Rather, ^1H NMR spectroscopy showed the presence of some free butene (and loss of $[\text{PtCl}_3(1\text{-butene})]^-$), which reversed following the end of photolysis (reaction carried out in a sealed system – reversible decomplexation).

Thus, a mechanism can be proposed as in Scheme 1, each step of which is based upon solid literature precedent. The upper half shows a photochemically induced reaction of $[\text{PtCl}_6]^{2-}$ with NBu_4^+ that activates the terminal carbon of a butyl chain to form a σ -alkyl complex **2**, leading to the zwitterionic η^2 -complex **3** *via* β -elimination.^{14a,28} Support for the proposed σ -alkyl intermediate comes from analogous photochemical reactions of $[\text{PtCl}_6]^{2-}$ with arenes (no β -hydrogen) where stable

σ -aryl complexes are formed,¹³ while support for **3** arises from the



Scheme 1: Proposed, indicative mechanism for the photochemical formation of **1**.

above experiment with PPN salts showing no reactivity of [PtCl₃(1-butene)] with [PtCl₆]²⁻.

The lower part of Scheme 1 then shows photoexcitation of [PtCl₆]²⁻ leading to Cl[•] (and Pt^{III}), which can then abstract a hydrogen from the β -position of the now functionalised alkyl group to give radical **4**. This extrudes alkene **5**, which reacts photochemically with [PtCl₄]²⁻ (from reduction of Pt^{III}) to give product **1**; proposing [•]NBU₃ is consistent with the observation of NBU₃H⁺ by liquid injection field desorption/ionisation mass spectrometry (requiring only proton abstraction in the medium). We also note that ‘consumption’ of two equivalents of Pt^{IV} requires the formation of a single equivalent of butadiene and so with NBU₄⁺ in excess, it is statistically most likely that each butadiene will result from activation of NBU₄⁺, which would require NBU₃H⁺ as the only nitrogen-containing product.

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Conflicts of interest

There are no conflicts to declare.

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