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Photochemistry of platinum phosphine complexes. Perspective in C–H bond activation

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This paper is respectfully dedicated to the memory of Professor Luigi M. Venanzi

Abstract

The photochemistry of the diphosphino Pt(II) hydrides [$LPtH_2$] (L = $(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2$ (**7**); L = $(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2$ (**8**);L = $(t\text{-}Bu)(Ph)P(CH_2)_2P(Ph)(t\text{-}Bu)$ (**9**)) is reported. The primary photoevent is the dissociation of H_2 and formation of the 14-e [LPt] species. These coordinatively unsaturated intermediates provide a versatile entry point into the C–H bond activation of hydrocarbons. [LPt] reacts with benzene in an oxidative addition reaction to yield [$LPt(H)(C_6H_5)$] complexes. The importance of the metal centre and ancillary ligation in the C–H bond activation is discussed. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Photolysis; Diphosphino Pt(II) hydride complexes; C–H bond activation

1. Introduction

The field of C–H activation developed from an interest in the homogeneous catalysis of a variety of alkane and alkene conversions by phosphine complexes of transition metals [1,2]. These are believed to involve an oxidative addition as the C–H bond breaking step, and may be either thermal or photochemical.

Metal olefine, metal hydride and metal carbonyl complexes with phosphines as ancillary ligands play a key role in the C–H bond activation sequences of a variety of important photochemical processes leading to alkane and alkene functionalisations [3,4]. As such, reach photochemistry of carbonyl, hydride and olefine complexes with phosphine ligands bound to Platinum(II) constitutes a critical entry point for the development of efficient C–H bond activation processes [4–6]. Indeed, extensive photochemical studies have been carried out on the above type of complexes proceeding via the even numbered, 14- and 16-electron Pt intermediates. The photochemical dissociation of ligands such as CO, H_2 or alkene has proved an excellent way of producing a coordinatively unsaturated metal centre capable of oxidatively adding a carbon–hydrogen bond of alkane or alkene. Phosphines are important ligands because they are among the few in which electronic and steric properties can be systematically manipulated to stabilise the metal fragment L_nPt ($L = PPh_3$, $n = 2$; L = P–CH_2–CH_2–P, $n = 1$) produced in situ by photodissociation of the one two electron (CO, $CH_2{=}CH_2$) or two one electron (H, alkyl, η^1-allyl) ligands [4].

In this paper, we have chosen to focus on the reactions of C–H bond activation with soluble synthetic Platinum complexes in homogeneous solution. We also focus primarily on photochemical production of reactive unsaturated fragments generated by loss of $CH_2{=}CH_2$ and H_2 ligands from Platinum phosphine complexes.

2. Experimental details

2.1. Photochemistry of platinum phosphine complexes

During the past decade our research group [3] has reported that irradiation of [$(PPh_3)_2PtC_2H_4$] (**1**) with 280 nm light induces ethylene dissociation (Eq. (1)).

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$$\underset{\mathbf{1}}{[(PPh_3)_2PtC_2H_4]} \xrightarrow[280\ \mathrm{nm}]{h\nu} \underset{\mathbf{2}}{[(PPh_3)_2Pt]} + C_2H_4 \qquad (1)$$

The 14 valence electron $[(PPh_3)_2Pt]$ (**2**) intermediate is quite reactive. In CH_2Cl_2 solution, the final product obtained was the complex $[(PPh_3)_2Pt(Cl)(CH_2Cl)]$, resulting from oxidative addition of CH_2Cl_2 to the 14 electron intermediate **2** [7]. However, irradiation of **1** with 254 nm light did not induce ethylene loss but rather orthometallation of one of the PPh_3 ligands forming the ethylene–hydride complex **3** (Eq. (2)).

$$\underset{\mathbf{1}}{[(PPh_3)_2PtC_2H_4]} \xrightarrow[254\ \mathrm{nm}]{h\nu} \underset{\mathbf{3}}{[(PPh_3)(Ph_2PC_6H_4)Pt(H)(C_2H_4)]} \qquad (2)$$

The hydrido complex **3** undergoes a secondary photoreaction forming the ethyl complex $[(Ph_3P)(Ph_2PC_6H_4)Pt(C_2H_5)]$ (**4**) as a result of photoinduced $CH_2{=}CH_2$ insertion in the Pt–H bond of complex **3**. At 280 nm, photodissociation of $CH_2{=}CH_2$ from **1** occurs at convenient rates in dichloromethane and ethanol.

The intermediate, $[(PPh_3)_2Pt]$ (**2**), does not react with C–H bonds of saturated or unsaturated hydrocarbons. Photolysis ($\lambda = 280$ nm) of **1** in mixed benzene–cyclohexane or benzene–cyclopentane solutions leads only to $[(PPh_3)_2Pt]_2$ as the platinum-containing reaction product. This result raises questions about whether a very suitable metal centre is required in order to induce intermolecular C–H activation. Independent work in Whitesides laboratory [8,9] demonstrates that thermal reductive elimination of neopentane from [*cis*-hydridoneopentyl(bis-dicyclohexylphosphinoethane)Pt] (**5**) produces the reactive intermediate [bis-dicyclohexylphosphinoethane]Pt and that this reacts with C–H bonds in saturated and unsaturated hydrocarbons. In somewhat related experiments, we observed that photolysis of **5** in cyclopentane gave the corresponding [LPt(cyclopentyl)H] complex **6** ($L = Cy_2P–(CH_2)_2–PCy_2$). Perhaps the most important discovery differentiating the photochemical activation and the thermal analog is its greater yield of oxidative addition product, most likely due to the fact that photolysis was carried out at a lower temperature.

This evidence along with molecular orbital considerations [1,10] suggest that electronic and steric properties of bent diphosphines are important factors that should increase intermolecular reactivity of Pt(0) species of the [(P–P)Pt] type (P–P = diphosphine), enabling access to C–H bond activation of hydrocarbons.

With this information in hand, we focused our attention on the photochemistry of dihydridediphosphine complexes of Pt(II): $[(t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2PtH_2]$ (**7**), $[(t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2PtH_2]$ (**8**), and $[(t\text{-}Bu)(Ph)P(CH_2)_2P(Ph)(t\text{-}Bu)PtH_2]$ (**9**).

The *cis*-dihydrides **7–9** were thermally stable even in solution at 90 °C and show no tendency to dissociation of the coordinate hydride.

It was encouraging to find that photolysis of **7–9** complexes in benzene led to dissociation of H_2 and the formation of $[LPt(H)(C_6H_5)]$ complexes **10–12** [(**10**) $L = (t\text{-}Bu)_2P(CH_2)_2P(t\text{-}Bu)_2$; (**11**) $L = (t\text{-}Bu)_2P(CH_2)_3P(t\text{-}Bu)_2$; (**12**) $L = (t\text{-}Bu)(Ph)P(CH_2)_2P(Ph)(t\text{-}Bu)$] as products of intermolecular C–H activation of C_6H_6. No orthometallation products were observed.

Hence, the formation of **10–12** must arise from highly reactive species of Pt(0) initially formed as a result of photoreductive elimination of H_2 from the Pt(II) diphosphinehydride (Eq. (3)).

$$\underset{\mathbf{7-9}}{[LPtH_2]} \xrightarrow[-H_2]{h\nu} [LPt] \xrightarrow{C_6H_6} \underset{\mathbf{10-12}}{[LPt(H)(C_6H_5)]} \qquad (3)$$

The [LPt] species are mononuclear chelate intermediates which are highly unsaturated, both coordinatively and electronically, and which could promptly abstract hydrogen from C_6H_6.

Elimination of H_2 proved to proceed in a concerted fashion since irradiation of an equimolecular mixture of **7** and $[LPtD_2]$ **7′** gave only H_2 and D_2, no HD being detected.

These crossover experiments indicate that reductive photoelimination of H_2 is strictly intramolecular. The electronic absorption spectra of **7–9** complexes revealed little regarding the nature of the photoreactive excited states since no well-resolved bands were observed in the 250–350 nm region.

The use of state correlation diagrams, which point to possible pathways interconnecting reactants and products [4,10,11], appears useful in rationalising the photoreactivity of the $[LPtH_2]$ considered. It is usually assumed that photodissociation is the consequence of exciting an electron from a bonding orbital to the corresponding antibonding orbital. In a qualitative energy-level scheme for the system $[LPtH_2]$ (assuming a pseudo-square planar coordination) the highest orbital $\sigma_{x^2-y^2}$ is the principal bonding orbital between H_2 and Pt, and the lowest unoccupied orbital $\sigma^*_{x^2-y^2}$ is strongly antibonding between the metal and H_2. Thus an active excited state involved in either depopulation of $\sigma_{x^2-y^2}$ or population of $\sigma^*_{x^2-y^2}$ can be suggested since either should greatly weaken the Pt–H_2 bonding.

In an attempt to extend the chemistry of $[LPtH_2]$ species to alkane C–H bond activation, we carried out the photolysis of the complexes **7–9** in cyclopentane solvent. Although photodissociation of the H_2 does take place, the [LPt] species does not react with the alkane under similar conditions used in C_6H_6. The major Platinum-containing products obtained are the dinuclear complexes [LPt–PtL] (**13**).

The results seem to indicate that the intermediate species [LPt] are fairly strong nucleophiles inert to an attack by alkane, thus enabling the formation of the dimer products.

It should be emphasised, however, that oxidative addition product [LPt(H)(R)] (R = alkyl)-resulting from H abstraction from the alkane solvent-would itself be expected to undergo a secondary photolysis of reductive elimination type. It would, therefore appear that the phosphine-stabilised platinum species [LPt] does not react intermolecularly with unactivated C–H bonds of alkane although it react easily with benzene. Recently Bercaw and co-workers [12] reported that sufficiently electrophilic cationic Pt(II) centres containing the *N*,*N*,*N*′,*N*′-tetramethylendiamine (TMEDA) ligand should be able to activate alkane C–H bonds.

3. Conclusion and perspectives

A high metal centre electrophilicity is clearly an essential requisite to make C–H bond activation of alkane feasible. Electrophilicity is a consequence not only of the chemical nature of the central metal and its oxidation state, but it is also tuned somewhat by the ancillary ligands bonded to it. In addition, it is also important that frontier orbital of correct symmetry in the central metal be available to accept the electrondensity of the C–H bond to be activated [13]. The general approach to C–H activation by oxidative addition commonly involves a low-valent transition metal with good donor ligands (hydride [1], Cp* [1,5], Tp*(hydrotrispyrazolylborate). This now seems to be a general reaction for hydride complexes with these ligands, indeed it has already been observed for compounds of Ir, Rh, and Pt [5,14,15].

4. Experimental

4.1. General data

All preparations and photochemical experiments were carried out under a dry argon atmosphere using standard Schlenk techniques. The solvents were dried by refluxing over the appropriate substrates and were distilled under argon prior to use.

The starting materials [$(PPh_3)_2PtC_2H_4$] (**1**), [$Cy_2P–(CH_2)_2–PCy_2Pt(H)R$] (**5**) (Cy = cyclohexyl; R = neopentyl), [$(t\text{-}Bu)_2P(CH_2)_nP(t\text{-}Bu)_2PtH_2$] (**7**, $n = 2$; **8**, $n = 3$) and [$(t\text{-}Bu)_2(Ph)P(CH_2)_2P(Ph)(t\text{-}Bu)_2PtH_2$] (**9**) were prepared as described in the literature [8,16].

Elemental analysis was performed by the Microanalytical Laboratory of the Department of Chemistry, University of Ferrara, Italy.

Photochemical reactions were performed with the output of a 500W Oriel Hg lamp fitted with an IR blocking filter and a water filter to remove excess heat. The appropriate wavelength of irradiation was obtained with an Applied Photophysics *f* 3/4 monochromator.

Analysis for H_2 by Gaschromatography was carried out by using a Perkin–Elmer F17 Gaschromatograph with a 5 Å molecular sieves column.

The NMR spectra were recorder on a Bruker AC 200 instrument and in part on an AMX 500 operating for ^1H at 200.13 (500.13) MHz and for ^{31}P at 81.0 (202.4) MHz. The chemical shift scales are relative to internal TMS for ^1H and to external H_3PO_4 for ^{31}P.

The FT-IR spectra were recorded on a Bruker IFSS88 FT-IR spectrometer.

UV–vis spectra were recorded with a JASCO-Uvidec 650 spectrophotometer.

*4.2. Photolysis of [$(PPh_3)_2PtC_2H_4$] (**1**)*

Compound **1** is a white compound with maximum absorption in benzene–cyclohexane(1:1) solution at 285 nm. Photolysis ($\lambda = 280$ nm) of **1** (10^{-2} M in benzene–cyclohexane) under argon results in the formation of a dark red solution. Irradiation was stopped after 50 min. Removal of the solvent under vacuum yielded a brown residue identified as [$(PPh_3)_2Pt$]$_2$ by ^1H- and ^{31}P-NMR [3].

^1H-NMR spectrum of the distillate showed the resonance of free C_2H_4. The same result was obtained in the photolysis of **1** in benzene–cyclopentane solution.

*4.3. Photolysis of [$Cy_2P–(CH_2)_2–PCy_2Pt(H)(CH_2–CMe_3)$] (**5**)*

The electronic spectrum of **5** in cyclopentane shows an absorption maximum at 235 nm and two shoulders at 278 and 300 nm.

A solution of **5** (0.15 mmol) in cyclopentane was irradiated for 1 h at 280 nm. During irradiation, a white precipitate formed. The solvent was removed in vacuo and the white product identified as [$Cy_2P–(CH_2)_2–PCy_2Pt(H)(C_5H_9)$] (**6**) by FT-IR and NMR (^1H and ^{31}P) spectra [8,9].

The yield of neopentane was quantitative as determined by GC. The yield of **6** was 75.8%.

*4.4. Photolysis of dihydride diphosphine Pt(II) **7**–**9**, in benzene*

A solution of complex **7** (0.20 mmol) in benzene was irradiated for 1 h at 280 nm. Analysis of the gases above the irradiated solution showed the presence of H_2. The solvent was removed in vacuo and the colourless residue (yield 72%) was identified as [$(t\text{-}Bu)_2P–(CH_2)_2–P(t\text{-}Bu)_2Pt(H)(C_6H_5)$] (**10**) by elemental analysis [C, calc. 44.67, Found: 44.52; H, calc. 7.78, Found: 7.65], FT-IR and ^1H-NMR spectra. FT-IR (nujol, cm^{-1}): ν(Pt–H) 1992. ^1H-NMR (CD_2Cl_2): δ 7.5 (t with Pt satellites, $J_{P–H} = 7.5$ Hz, $J_{Pt–H} = 58.2$ Hz, 2H), 7.02 (t, $J_{P–H} = 7.5$ Hz, 2H), 6.70 (t, $J_{P–H} = 7.5$ Hz, 1H),

− 1.12 (dd with Pt satellites, $J_{P\text{–}H} = 20$ Hz, $J_{P'\text{–}H} = 190$ Hz, $J_{Pt\text{–}H} = 1165$ Hz, 1H).

The photolysis of complexes **8**, **9** were performed as described for complex **7**. H_2 was evolved and the phenylhydrido complexes **11** and **12** were obtained (the yield was 70%). Apart from the changes due to the presence of different diphosphines, the FT-IR and ^{1}H-NMR spectra were as for **10**.

Photolysis of an equimolar amount of **7** and **7**-d_2 in benzene was carried out as described for **7**. Analysis of the gases above the irradiated solution showed only H_2 and D_2.

4.5. Photolysis of dihydride diphosphine Pt(II) ***7–9****, in cyclohexane or in cyclopentane*

These were performed as described for irradiation in C_6H_6. Photoinduced elimination of H_2 was obtained. Removal of the solvent from the irradiated solution gave a red compound identified by ^{1}H- and ^{31}P-NMR spectra as $[(t\text{-}Bu)_2P\text{–}(CH_2)_2\text{–}P(t\text{-}Bu)_2Pt]_2$ [16].

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