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REDUCTIVE ELIMINATION OF 1,3-DI-*p*-TOLYLTRIAZENE IN REACTIONS OF *trans*-[Pt(PPh₃)₂H(*p*-CH₃C₆H₄N=N=NC₆H₄CH₃-*p*)] WITH CO, 2,6-Me₂C₆H₃NC, PPh₃, AND PhC≡CPh

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Summary

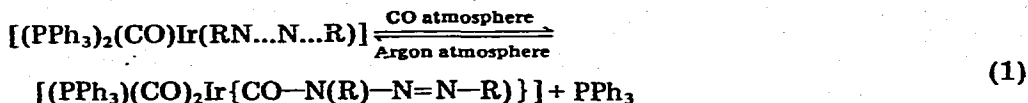
The hydrido-1,3-di-*p*-tolyltriazenido complex of platinum(II) *trans*-[Pt(PPh₃)₂-H(*p*-CH₃C₆H₄N=N=NC₆H₄CH₃-*p*)] reacts with CO, 2,6-Me₂C₆H₃NC, PPh₃ and PhC≡CPh under mild conditions to yield platinum(0) complexes by reductive elimination of 1,3-di-*p*-tolyltriazene.

Introduction

Most of the work on transition metal-triazenido complexes has been focused on the coordinating properties of the triazenido ligand. It has been proved by X-ray investigations that the ligand can act as monodentate [1–5], or bidentate [1, 6–8], or as a ligand bridging two metal centers [9–13]. Compounds of the type [L₂(CO)MM'(RN≡N≡R')X] (obtained by treating L₂(CO)MX with M'(RN≡N≡NR')) (L = PR₃; M = Rh, Ir; M' = Cu, Ag; R, R' = alkyl or aryl groups; X = halogen) contain a five-membered ring in which a M-to-M' donor bond is bridged by an azenido group [14–16]. Moreover, reactions of L₂(CO)MXⁿ with X'Hg(RN₃R') or Hg(RN₃R')₂ (R' = CH₃, *p*-tolyl; R = CH₃) gave M–Hg bonded compounds in most cases, in which the triazenido group can bond (i) as a M–Hg bridging ligand, (ii) as an acyltriazenido chelating group, or (iii) by chelating the metal M. The type of structure formed is critically dependent on the nature of M, X, and the groups R and R' [17].

Recent work has also been directed towards the reactions of the azenido ligand with carbon monoxide. It has been found that acyltriazenido-metal compounds can be formed by CO insertion. For example, CO at 1 atm reacts

reversibly with $[(PPh_3)_2(CO)Ir(RN\cdots N\cdots NR)]$, according to reaction 1 [16].



(R = *p*-tolyl)

In all cases here presented, the reactions of the triazenido group are characterized by the fact that it remains coordinated to a metal atom even if it is displaced from M' to M ; in reactions with CO it remains coordinated, eventually as an acyl-triazenido ligand.

Another interesting case is represented by reaction 2 in which the triazene molecule is displaced from the metal [18].



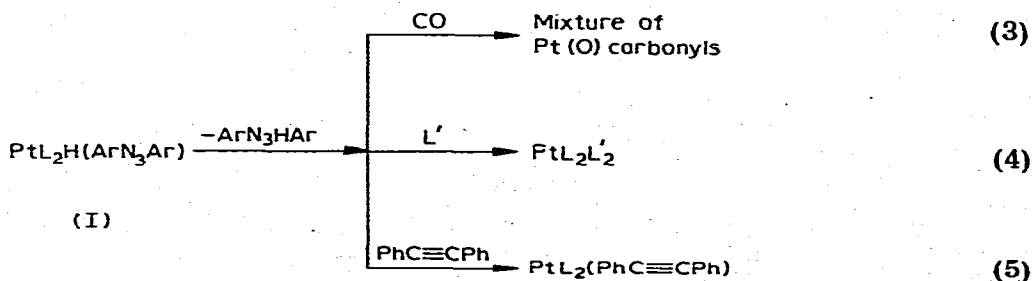
(I)

(TCNE = tetracyanoethylene; dtt = 1,3-di-*p*-tolyltriazenido anion, *p*-CH₃C₆H₄N=N=NC₆H₄CH₃-*p*)

If the resulting complex can be viewed as a platinum(0) species, reaction 2 provides one of the earlier examples of reductive elimination [19,20]. Continuing our investigations on the mode of coordination of the triazenido ligand and on the reactions of complex I [2-5,13,18,21], we describe other reactions with CO, 2,6-Me₂C₆H₃NC, PPh₃, PhC≡CPh, all of them involving reductive elimination of the triazene molecule.

Results and discussion

Complex I [18] reacts with CO, 2,6-Me₂C₆H₃NC, PPh₃, or PhC≡CPh during 30 min at 20–50°C with reductive elimination of Hdtt and formation of platinum(0) complexes, as in eq. 3–5.



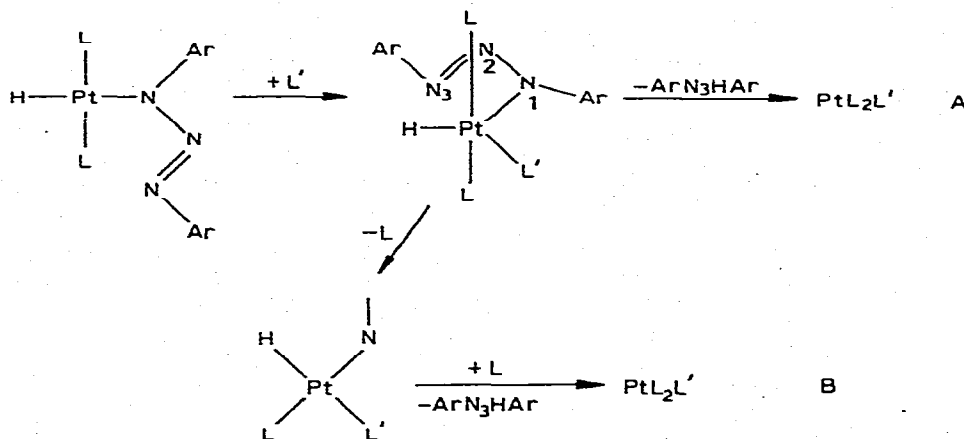
(I)

L' = L or 2,6-Me₂C₆H₃NC

The reaction with CO occurs even at room temperature and leads to a mixture of platinum(0) carbonyls which have been identified by their IR spectrum: two absorption bands of strong intensity at 1948 and 1983 cm⁻¹ and a weak band at 1912 cm⁻¹ are assignable to $[Pt(PPh_3)_2(CO)_2]$ [22], and bands at 1820, 1800,

and 1795 cm^{-1} are assignable to a platinum(0) complex with triphenylphosphine and bridging carbonyl ligands [23,24]. Thus this reaction parallels that occurring with *trans*-[Pt(PPh₃)₂H(C₃H₆CN)] [25] and contrasts with the other possibility which leads to an acyltriazenido derivative [16] by CO insertion into the Pt–N bond.

Reaction 3 may involve coordination of CO with formation of a five-coordinated intermediate having the triazenido and the hydride ligands in adjacent positions which favors their interaction, leading to the reductive elimination of the triazene molecule.



$L' = \text{CO}, \text{PPh}_3, 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}, \text{PhC}\equiv\text{CPh}$

The interaction might involve either the coordinated nitrogen or N₃; the latter interaction would be possible since it is likely that the triazenido moiety retains a geometry which leads to a short Pt–N₃ distance, as found by X-ray studies on complex I [3], *cis*-[Pt(PPh₃)₂Cl(dtt)] [4], *trans*-[Pd(PPh₃)₂Cl(dtt)] [5], and *cis*-[Pt(PPh₃)₂(dpt)₂] [1].

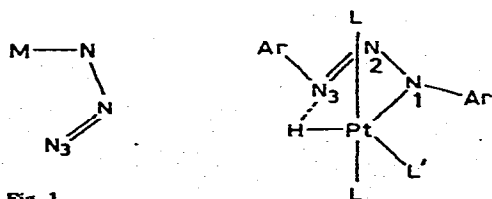


Fig. 1.

A possible alternative mechanism, involving an acyltriazenido intermediate, involves either an insertion of CO into the Pt–N bond or attack of the uncoordinated nitrogen atom on the CO. The postulated intermediate would undergo reductive elimination yielding the resulting Pt(0) carbonyl complexes.

Reaction 4 ($L' = 2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC}$) was carried out by treating a suspension of the triazenido complex in *n*-heptane with an excess of isocyanide. The result-

ing yellow complex was identified as the known [26] platinum(0) complex $[\text{Pt}(\text{PPh}_3)_2(2,6\text{-Me}_2\text{C}_6\text{H}_3\text{NC})]_2$. The IR spectrum shows a strong band at 1995 cm^{-1} indicative of an isocyanide ligand coordinated to Pt(0); the ^1H NMR spectrum shows absorptions at δ 7.7–8.6(m, br) and 2.02(s) ppm in the ratio 40 : 12.

The conclusions reached for the mechanism of reaction 3 may hold also for reaction 4 ($\text{L}' = \text{isocyanide}$). In the latter case it should be noted that although isocyanide insertion into a Pt–H bond is well documented [26] this reaction does not occur with complex I, the reductive elimination of the triazene molecule taking place.

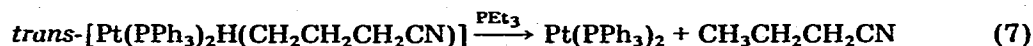
A different mechanism involving the four-coordinate intermediate $[\text{Pt}(\text{PPh}_3)(\text{CNR})\text{H}(\text{CH}_2\text{CN})]$ was proposed for the reductive elimination of a cyanoalkane in reaction 6.



The intermediate which is formed by substitution of a PPh_3 molecule, was isolated and characterized: it has adjacent Pt–H and Pt–C bonds in the *cis* positions which can interact with elimination of CH_3CN to give the final platinum(0) complex [26]. Reactions 3–5 might occur by the analogous mechanism B.

Reaction 4 with $\text{L}' = \text{PPh}_3$ occurs at ca. 35°C , and involves elimination of the triazene molecule with formation of the platinum(0) complex $\text{Pt}(\text{PPh}_3)_4$ [28]. In this case no insertion into a Pt–N bond is possible.

It is interesting to compare reaction 4 ($\text{L}' = \text{PPh}_3$) with that in eq. 7.

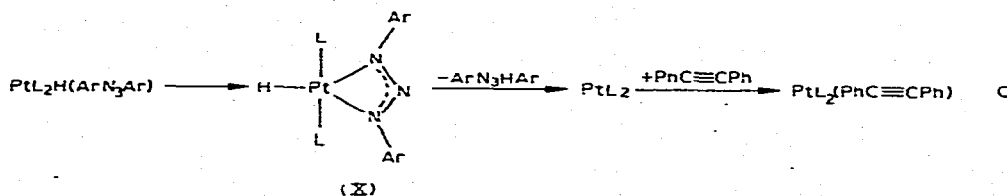


In this case the phosphine PEt_3 promotes reductive elimination of the cyanoalkane but no extra molecule of phosphine is incorporated into the final platinum(0) complex [25].

The displacement of the triazene molecule by $\text{PhC}\equiv\text{CPh}$ (reaction 5) does not occur as easily as in the other cases, since the reaction must be carried out at ca. 50°C for ca. 20 min; pale yellow crystals of $[\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh})]$ are isolated almost quantitatively [32].

Comparison of reactions 2–5 with those involving *trans*- $[\text{Pt}(\text{PPh}_3)_2\text{HCl}]$ in place of complex I, suggests that the reductive elimination of the triazene molecule occurs more easily than that of HCl. In fact, only with TNCE does the hydride–chloride complex react by elimination of HCl [33], while with CO and PPh_3 only displacement of Cl^- occurs, with formation of cationic complexes of the type *trans*- $[\text{Pt}(\text{PPh}_3)_2\text{HL}]^+$ [34,35].

It is relevant to note that $\text{PhC}\equiv\text{CPh}$ is not particularly reactive towards Pt(II) complexes (though it does react when a coordination site on the plane of the Pt(II) species is readily available [36]). Thus the fact that the triazene molecule is displaced by $\text{PhC}\equiv\text{CPh}$ is surprising, and suggests that the reaction occurs by initial reductive elimination of the triazene molecule to form the coordinatively unsaturated $\text{Pt}(\text{PPh}_3)_2$ species [29], which would easily coordinate the $\text{PhC}\equiv\text{CPh}$ molecule to yield the final complex, as in the following scheme:



This possibility may be associated with the fact that the triazenido complex displays fluxional behaviour which leads to equivalence of the two nitrogen atoms bearing the tolyl groups via a five-coordinate intermediate of the type X [2,18] which has the hydrido ligand and the coordinated nitrogen atoms in adjacent position which favours their interaction, thus facilitating reductive elimination of the triazene molecule. However, it should be pointed out that the fluxional behaviour is not influenced by the presence of added uncoordinated triazene [2], thus the dissociation of the triazene molecule from the hydride complex is unlikely. Reaction 5 probably occurs readily because of the large *trans* influence of the hydride ligand on the coordinated nitrogen, and also because the supposed N₃-hydride interaction (see Fig. 1).

Experimental

Solvents were dried and purged with nitrogen before use; IR and ¹H NMR spectra were recorded on a Perkin-Elmer 457 and on 90 MHz Bruker HFX-10 instrument. 1,3-Di-*p*-tolyltriazene (Hdtt) [30], *cis*-[Pt(PPh₃)₂Cl₂] [31], *trans*-Pt(PPh₃)₂H(dtt) [18], Pt(PPh₃)₂(PhC≡CPh) [32] were prepared by published methods.

Reaction of *trans*-[Pt(PPh₃)₂H(dtt)] (I) with CO

Carbon monoxide was bubbled at room temperature through an ethanol suspension of complex I (100 mg in 5 ml). After a few minutes the yellow suspension turned yellow-gray. The carbon monoxide was bubbled through until the suspension began to darken. The product was filtered off. Elemental analysis showed the absence of nitrogen. The IR spectrum showed $\nu(\text{C}\equiv\text{O})$ bands in the 2000–1800 cm⁻¹ region, indicating the presence of a mixture of Pt(0) carbonyls.

Reaction of I with 2,6-Me₂C₆H₃NC

50 mg of complex I, suspended in 2 ml of *n*-heptane was treated with 20 mg of 2,6-Me₂C₆H₃NC for 30 min at ca. 30°C. The yellow precipitate was filtered off, and identified as Pt(PPh₃)₂(2,6-Me₂C₆H₃NC)₂. Found: C, 65.93; H, 4.71; N, 2.98. C₅₄H₄₈N₂P₂Pt calcd.: C, 66.04; H, 4.93; N, 2.85%.

Reaction of I with PPh₃

An ethanol suspension of I (5 ml, 100 mg) was treated with 100 mg of PPh₃ at ca. 30°C, under nitrogen. The initial yellow suspension did not significantly change colour. During ca. 30 min a bright yellow complex had formed, whose elemental analysis showed absence of nitrogen and agreed with Pt(PPh₃)₄. Found: C, 69.3; H, 4.75. C₇₂H₆₀P₄Pt calcd.: C, 69.5; H, 4.86%.

Reaction of I with $\text{PhC}\equiv\text{CPh}$

An ethanol suspension of I (5 ml, 100 mg) was treated with 50 mg of $\text{PhC}\equiv\text{CPh}$ at ca. 50°C under nitrogen. The yellow colour slightly faded, and crystals separated. After ca. 30 min the volume of the suspension was reduced to ca. 2 ml by bubbling nitrogen vigorously through it. The pale yellow crystals were filtered off. The elemental analysis showed the absence of nitrogen and was consistent with $\text{Pt}(\text{PPh}_3)_2(\text{PhC}\equiv\text{CPh})$. Found: C, 67.1; H, 4.30. $\text{C}_{50}\text{H}_{40}\text{P}_2\text{Pt}$ calcd.: C, 66.9; H, 4.49%.

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