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PHOTOINDUCED REDUCTIVE ELIMINATION OF CYANOALKANES FROM HYDRIDOCYANOALKYL COMPLEXES OF PLATINUM(II)

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Summary

The photoinduced reductive elimination of cyanoalkanes (CH_3CN, CH_3CH_2CN and $CH_3(CH_2)_2CN$) from *trans*-hydridocyanoalkyl complexes of platinum(II), $[PtH(R)(PPh_3)_2]$ (R = CH_2CN, $(CH_2)_2CN$, $(CH_2)_3CN$) has been studied. The three *trans* complexes undergo isomerization to *cis* forms in the initial step before the reductive elimination. The elimination from the *cis* isomers is intramolecular as shown by the absence of crossover with the $[PtH(CH_2CN)(Ph_2PCH{\equiv}CHPPh_2)]$ analogue and of the failure to detect the presence of free radicals during the reaction. The monomeric $[Pt(PPh_3)_2]$ complex has been identified as the initial product of reductive elimination. Several reactions of this mechanistically important compound are also described.

Introduction

Much interest attaches to both the preparative and mechanistic aspects of the reductive elimination of alkanes from *cis*-hydridoalkylmetal complexes [1], particularly in view of the catalytic potential of these complexes [2]. The chemistry of hydridocyanoalkyl derivatives, $[PtH(R)(PPh_3)_2]$ (R = CH_2CN, $(CH_2)_2CN$, $(CH_2)_3$-CN), has been studied extensively in recent years [3].

Cyano-substituted alkyl groups enforce a *trans* configuration on the complexes and provide steric protection for the hydrido ligands. We show below that intramolecular reductive elimination of cyanoalkanes can be achieved by photolysis of *trans*-hydridocyanoalkylplatinum(II) toluene solutions, and that this provides a useful method of generating the reactive $[Pt(PPh_3)_2]$ species in situ.

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Experimental

Materials. The starting complexes [PtH(R)(PPh$_3$)$_2$] (Ia, R = CH$_2$CN; IIa, R = (CH$_2$)$_2$CN; IIIa, R = (CH$_2$)$_3$CN) were prepared as described in the literature [3]. The *trans* configuration was confirmed by the ^{1}H and ^{31}P NMR spectra [3]: Ia: δ(H) -7.32 ppm (tt); δ(P) 32.2 ppm(s); IIa: δ(H) -4.50 ppm(t), δ(P) 35.2 ppm; IIIa: δ(H) -4.51 ppm(t), ^1J(Pt–H) 635 Hz, ^2J(P–Pt–H) 18 Hz; δ(P) 35.1 ppm(s), ^1J(Pt–P) 3162 Hz.

NMR Studies. ^{31}P NMR measurements were carried out with a Bruker WH90 spectrometer equipped with thermostat. ^{1}H NMR data at 90 MHz were obtained with a Bruker WH90 spectrometer and those at 220 MHz with a Perkin–Elmer R34 instrument.

ESR Studies. The ESR experiments were carried out with a Bruker model ER 200tt spectrometer. When a carefully degassed toluene solution of Ia containing phenyl-t-butylnitrone as spin trap was irradiated in the cavity of ESR spectrometer there was no evidence of trapped radicals ($\cdot$H or $\cdot$CH$_2$CN).

Mass spectra were obtained on a AEI MS902 mass spectrometer and GLC analyses with Perkin–Elmer 990 gas chromatograph.

General irradiation procedures

Photolysis experiments were carried out by the standard technique previously described [4], but using an additional quartz UV irradiation cell which allowed the solutions to be changed under a controlled atmosphere.

Photolysis of platinum(II) hydridocyanoalkyl complexes: Ia, IIa, IIIa

Photolysis (1 h) of degassed toluene solutions of Ia, IIa, IIIa with λ 313 nm caused a change from colorless to orange. Evaporation of the solvent from the solutions gave a cream-coloured solid. This was identified as the dimer [5] [Pt(PPh$_3$)$_2$]$_2$ (IVa) by its melting point, molecular weight, spectral data and elemental analysis: m.p. 248°C; mol. wt. 1434 in C$_6$H$_6$; mass spectrum (parent ion *m/e* 1438, fragment ion 719); ^{31}P NMR complex resonances centered at 54 ppm downfield from H$_3$PO$_4$. GLC analysis showed the presence in the distillate of CH$_3$CN, CH$_3$CH$_2$CN, and CH$_3$(CH$_2$)$_2$CN for Ia, IIa and IIIa, respectively. Prolonged photolysis (4 h) of degassed toluene solutions of Ia, IIa and IIIa with λ 334 nm caused bleaching of the initially generated orange color. The mixture was distilled under reduced pressure. GLC analysis showed the presence of three corresponding cyanoalkanes, as in the case of irradiation at 313 nm. Recrystallization from toluene/n-hexane of the residue from the distillation gave a red-orange product. The molecular weight and infrared spectrum (new absorption at 730 cm^{-1}, indicative of the presence of *ortho*-metallated phenyl group), were consistent with the cluster [Pt(C$_6$H$_4$PPh$_2$)(PPh$_2$)]$_3$ (Va) [6].

Photolysis of [Pt(PPh$_3$)$_2$]$_2$

The dimer [Pt(PPh$_3$)$_2$]$_2$ was irradiated at 77 K in an EPA glass. The irradiation was conducted through a clear Pyrex dewar vessel filled with liquid nitrogen. When the dimer was irradiated (λ 366 nm) the initial cream-colour disappeared. When the photolyzed sample was allowed to warm to room temperature the original colour, associated specifically with the low energy Pt–Pt absorption returned. When the sample was then recooled to 77 K the cream colour persisted and upon excitation it showed the characteristic π–π^* emission [7,8] of the $[Pt(PPh_3)_2]$ at 440 nm.

Low temperature glass irradiation

The complex *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ (Ia), was dissolved in a 12/1 EPA/chloroform * mixture and placed in an NMR tube with a round bottom. The solution was then cooled with liquid nitrogen in an unsilvered Pyrex dewar vessel to yield a clear glass-like substance. Irradiation was conducted by placing the Dewar vessel in front of a 200-W Xe-Hg point source lamp (λ 313 nm).

At 183 K the ^1H and ^{31}P NMR measurements of the irradiated sample gave: ^1H NMR: Pt–H, $\delta - 2.2$ (1H, dd, J(Pt–H) 1210, J(P^1–H) 202, J(P^2–H) 24.1 Hz; Pt–CH_2CN, δ 1.45 (2H, td, J(Pt–H) 67.5, J(P^1–H) 7.0, J(P^2–H) 10.5 Hz). ^{31}P NMR: $\delta(P_1)$ 31, $\delta(P_2)$ 29.5, (J(Pt–P_1) 1860, J(Pt–P_2) 2012, $J(P_1–P_2) = 10.2$ Hz). Both ^1H and ^{31}P NMR spectra showed that the platinum phosphine hydride was entirely in the *cis* form [9]. On warming the irradiated sample the *cis* isomer decomposed to yield $[(PPh_3)_2Pt]_2$ and CH_3CN (identified by ^{31}P NMR spectroscopy and GLC-MS analysis, respectively). Very similar results were obtained with the *trans* complexes IIa and IIIa.

Mechanistic studies

Attempts were made to assess the roles of inter- and intra-molecular pathways in the photochemically induced reductive elimination from the complexes Ia, IIa and IIIa.

Photolysis in toluene of a 1/1 (molar) mixture of *trans*-$[PtH(CH_2CN)(PPh_3)_2]$ and *trans*-$[PtH(CH_2CN)(Ph_2PCH{\equiv}CHPPh_2)]$ gave a ^{31}P NMR spectrum indicating 95% conversion into $[Pt(PPh_3)_2]_2$ and $[Pt(Ph_2PCH{=}CHPPh_2)]_2$, with no resonances consistent with the formation of mixed platinum(0) complexes.

Kinetics

The rate of cyanoalkane photoelimination was followed by monitoring the disappearance of the Pt–H protons in the ^1H NMR spectrum. This was accompanied by the appearance of the signal from the dissolved cyanoalkanes. After an induction period, corresponding to the *trans-cis* photoisomerization, the kinetic plot was linear. During the induction period no appreciable amount of cyanoalkanes was generated. Kinetics runs were also performed in the presence of 1 equivalent of added PPh_3. The rate of photoelimination was unaffected and evaporation of the solvent from toluene solutions of Ia, IIa and IIIa at the end of the photolysis (2 h) gave $[Pt(PPh_3)_3]$ quantitatively.

Photochemical reactions of $[PtH(CH_2CN)(PPh_3)_2]$ (Ia) with Lewis base ligands

$Pt(CNCH{=}CHCN)(PPh_3)_2$ (VIa). To a toluene solution (25 ml) of Ia (19 mg) in a Vycor reaction tube was added CNCH=CHCN (180 mg). After irradiation (λ 313 nm) for 2 h the volatile materials were distilled off under reduced pressure. GLC analysis showed the presence of CH_3CN in the distillate. Recrystallization of the residue from CH_2Cl_2/n-heptane gave VIa: ^1H NMR (C_6D_6) δ 7.54 (d, 2, J(P–H) 6.5 Hz, J(Pt–H) 60 Hz. IR (Nujol mull) ν (CN) 2200 cm^{-1}.

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* EPA = ethanol, isopentane, ether (2/5/5).

Pt(PhC≡CPh)(PPh$_3$)$_2$ (VIIa). This compound was prepared in a manner similar to VIa by the photoreaction (2 h) of Ia (19 mg) in the presence of PhC≡CPh (89 mg). After irradiation the volatile material was distilled off under reduced pressure. GLC analysis showed the presence of CH_3CN in the distillate. Recrystallization of the residue gave VIIa which was identified by its infrared spectrum, melting point and mass spectrum: IR (Nujol) 1740(s) cm^{-1}; m.p. 162–165°C; mass spectrum *m/e* (70 eV) 178(vs). The Ia complex did not react with the free ligands CNCH=CHCN and PhC≡CPh in the absence of light.

Discussion

The results reported here demonstrate that elimination of cyanoalkanes from *trans*-hydridocyanoalkylplatinum(II) complexes, Ia, IIa and IIIa can be photoinduced. The mechanism of the photoelimination reaction is of must interest. It has been shown that thermal elimination of biaryl from *cis*-diarylbis(phosphine)-platinum(II) complexes [10] proceeds in a concerted fashion, and photochemical elimination of cyanoalkanes from Ia, IIa and IIIa complexes probably occurs by a similar mechanism. Our experiments were directed towards determining the principal photoreaction pathway and establishing the nature of the related reactions. The low temperature results indicate that the *cis*-isomers are produced according to eq. 1:

$$trans\text{-}[PtH(R)(PPh_3)_2] \xrightarrow[a]{h\nu} cis\text{-}[PtH(R)(PPh_3)_2] \xrightarrow{b} [Pt(PPh_3)_2] + RH \qquad (1)$$

$$(RH = CH_3CN\ (Ia),\ CH_3CH_2CN\ (IIa),\ CH_3(CH_2)_2CN\ (IIIa))$$

Decomposition of the *cis* isomers occurs upon warming to room temperature yielding $[Pt(PPh_3)_2]_2$ and cyanoalkanes. When the reductive elimination of cyanoalkanes from complexes Ia, IIa and IIIa was monitored by following the disappearance of the ^1H resonances of the hydride ligand an induction period was observed during which no appreciable amount of cyanoalkanes was generated, suggesting that *trans-cis* isomerization occurs before reductive elimination. These isomerization (and kinetic) experiments suggest that the groups to be coupled must occupy *cis* positions and that process a of eq. 1 is the rate-determining step. Attempted crossover experiments showed that no intermolecular phosphine exchange took place prior to or during the photolysis. Thus in solutions, as in EPA glasses, the reductive elimination of cyanoalkanes occurs in a concerted fashion, and free radicals are apparently not present for any length of time during the reaction. Further support for unimolecularity is provided by the observation that PPh_3 does not affect the rate of cyanoalkane elimination.

A satisfactory mechanistic study requires all the reaction products to be accounted for. Although, as shown above, important information can be obtained from crossover and kinetic experiments, the resulting platinum-containing species are also of interest. The initial reductive elimination product is the monomeric 14-valence electron species, $[Pt(PPh_3)_2]$. The final product obtained by photolysis at 313 nm is the dinuclear complex $[Pt(PPh_3)_2]_2$. Failure to isolate the monomer $[Pt(PPh_3)_2]$ probably reflects the strong tendency of this species to form polynuclear compounds such as $[Pt(PPh_3)_2]_2$ or to undergo an *ortho*-metallation.

The formation of $[Pt(C_6H_4PPh_2)(PPh_2)]_3$ suggests that the dinuclear compound $[Pt(PPh_3)_2]_2$ undergoes metal–metal bond cleavage with subsequent *ortho*-metallation of one of the PPh_3 ligands. Irradiation at 77 K of the $[Pt(PPh_3)_2]_2$ dimer indicates that the metal–metal bond can be ruptured photochemically. The colour changes and the observed emission at 440 nm are those of $[Pt(PPh_3)_2]$. When the sample is allowed to warm to room temperature, the mixture takes on the cream colour associated with the low energy of Pt–Pt absorption and if the sample is then irradiated again the red colour of the *ortho*-metallated complex Va slowly appears. It is reasonable to suggest, therefore, that photocleavage of Pt–Pt absorption even occurs in a solid matrix, but that the rigid medium prohibits the dimerization of the $[Pt(PPh_3)_2]$ species. Hence, a second pathway (*ortho*-metallation) is made available for the photochemical production of the cluster Va. Evidence of the initial production of $[Pt(PPh_3)_2]$ in the elimination reaction comes from the finding that irradiation of Ia in the presence of $CNCH{=}CHCN$ and $PhC{\equiv}CPh$ leads to the formation of $Pt(CNCH{=}CHCN)(PPh_3)_2$ and $Pt(PhC{\equiv}CPh)(PPh_3)_2$. These reactions do not occur thermally, and $Pt(CNCH{=}CHCN)(PPh_3)_2$, $Pt(PhC{\equiv}CPh)(PPh_3)_2$ compounds must thus be formed by trapping of the $[Pt(PPh_3)_2]$ by $CNCH{=}CHCN$ and $PhC{\equiv}CPh$.

Further studies involving the reductive elimination–oxidative addition photoreactions, including extensions to other hydridometal complexes, are in progress.

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