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Preliminary communication

Photochemical rearrangement of tetracyanoethylene bis(triphenylphosphine)-platinum

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SUMMARY

Irradiation of a solution of $[Pt(PPh_3)_2(TCNE)]$ at 313 nm gives the novel percyano-vinylplatinum complex $[Pt(PPh_3)_2\{C(CN){=}C(CN)_2\}(CN)]$.

Tetrakis(triphenylphosphine)platinum(0) reacts with electronegatively-substituted olefins in apolar solvents to give complexes of the type $[Pt(PPh_3)_2(\text{substituted olefin})]$[1]. The nature of the olefin markedly affects the stability of these compounds. Thus, $[Pt(PPh_3)_2(C_2Cl_4)]$ gives the perchlorovinyl derivative $[Pt(PPh_3)_2(ClC{=}CCl_2)Cl]$ on refluxing in ethanol, whereas the tetracyanoethylene (TCNE) complex, $[Pt(PPh_3)_2(TCNE)]$ is recovered unchanged after refluxing in ethanol[1], chloroform or dichloromethane. Tetrakis(triphenylphosphine)platinum(0) reacts with TCNE to give $[Pt(PPh_3)_2(CN)_2]$, which was believed[2] to be formed via thermal rearrangement of the initially produced percyanovinyl derivative, $[Pt(PPh_3)_2\{NCC{=}C(CN)_2\}(CN)]$. A 3 h irradiation of an aged sample of $[Pt(PPh_3)_2(NCC{=}CCN)]$ with a sun lamp produces the cyano–acetylido complex $[Pt(PPh_3)_2(C{\equiv}CCN)(CN)]$ as a result of a photochemical rearrangement[3].

We have now found that a solution of $[Pt(PPh_3)_2(TCNE)]$ in $CHCl_3$ is sensitive to irradiation in the region of its high intensity UV absorption bands; the observed spectral changes are shown in Fig. 1A (complex conc. $3 \cdot 10^{-5}$ *M*). Irradiation of $[Pt(PPh_3)_2(TCNE)]$ (10^{-2} *M*) at 313 nm followed by removal of solvent gives a yellow-brown solid, which can be recrystallized from ethanol. Its IR spectrum in the range 1500–2300 cm^{-1} shows bands at 1590 m, 2145 w, 2130 m, and 2190 m cm^{-1}. No band at 2220 cm^{-1}, characteristic of the starting complex, is observed. These results indicate that a photochemical isomerization of the tetracyanoethylene complex to the novel percyano-vinyl derivative (I) has taken place.

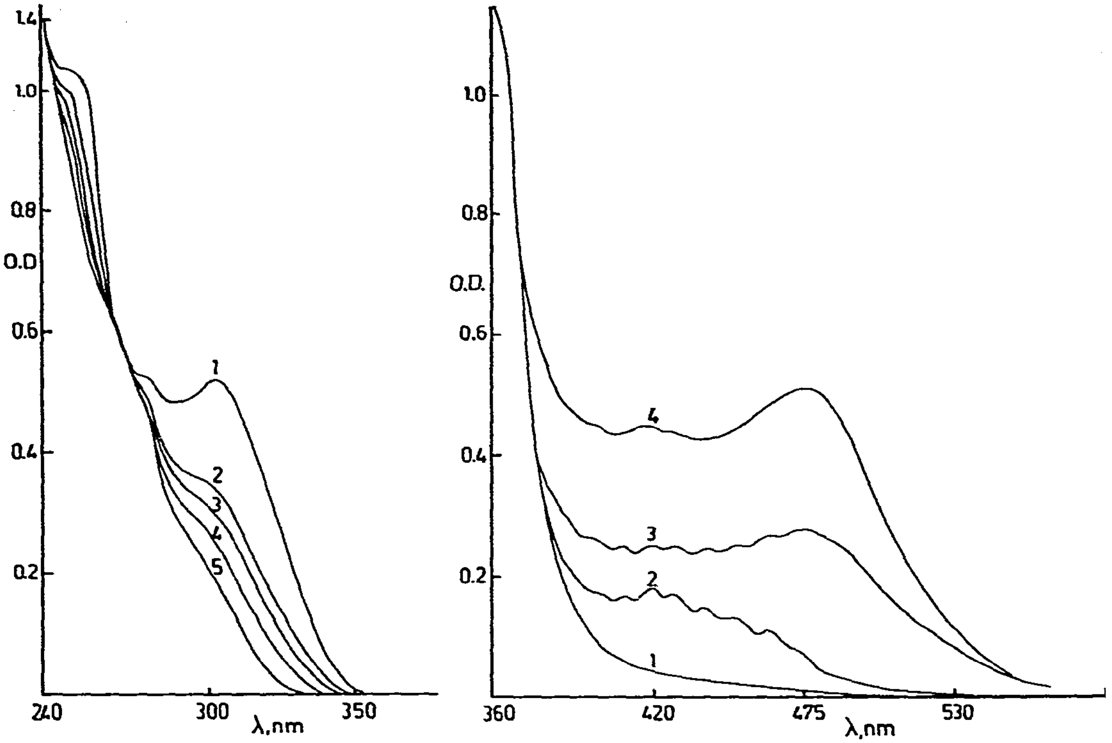
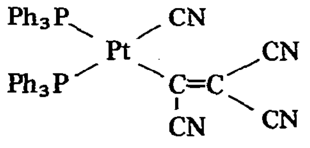


Fig. 1A. Spectral changes of $3 \cdot 10^{-5}$ *M* [Pt(PPh$_3$)$_2$(TCNE)] in chloroform; 1, before irradiation at 313; 2, 3, 4, 5, after irradiation for 10, 15, 20, 60 min, respectively.

Fig. 1B. Spectral changes of 10^{-2} *M* Pt(PPh$_3$)$_2$(TCNE) in chloroform solution for irradiation at 313 nm. Numbers refer to irradiation time in hours.



(I)

Evidence for the stepwise sequence in the photoreaction comes from the variation with time of the electronic spectrum of [Pt(PPh$_3$)$_2$(TCNE)] in concentrated solution (10^{-2} *M*; Fig. 1B). After irradiation for some hours two broad fully developed bands centered at 420 and 475 nm appear. The higher frequency band is assigned to the radical anion TCNE$^{\overline{\cdot}}$ on the basis of the ten-peak fine structure in concentrated chloroform solution (10^{-2}–10^{-1} *M*; λ_{max} 385, 390, 398, 405, 415, 425, 435, 448, 455, 467 nm). This spectrum corresponds to the stable TCNE$^{\overline{\cdot}}$ obtained on treatment with a reducing agent (*e.g.* Cu) in acetonitrile[4]. The fine structure of the 420 nm band vanishes after a relatively short irradiation time while the intensity of the other band increases. This