Laser Flash Photolysis of Hydridotetrakis(diethyl phenylphosphonite)cobalt(I). Direct Evidence for the Existence of a Co-ordinatively Unsaturated Species

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A transient species (λ_{max}: 580 nm, ε: 1.7×10^3 dm^3 mol^{-1} cm^{-1}) observed 0.43 μs after nitrogen laser pulse excitation of hydridotetrakis(diethyl phenylphosphonite)cobalt(I) in cyclohexane has been identified as a co-ordinatively unsaturated species, to which diethyl phenylphosphonite and hex-1-ene co-ordinate with second-order rate constants of 1.4×10^8 and 1.1×10^8 dm^3 mol^{-1} s^{-1} respectively.

Hydridocobalt complexes containing phosphorus ligands are used as catalysts in hydrogenation,[1—4] oligomerization,[1,5] and isomerization of olefins.[1,6,7] In these reactions, co-ordinatively unsaturated species have been assumed to maintain one catalytic cycle.

By means of laser flash photolysis, we have obtained direct evidence for the existence of a co-ordinatively unsaturated species, and the rate constants for the co-ordination of a phosphorus ligand and an olefin to this species have been determined.

Hydridotetrakis(diethyl phenylphosphonite)cobalt(I), $HCoL_4$, has been reported to induce exchange of phosphorus

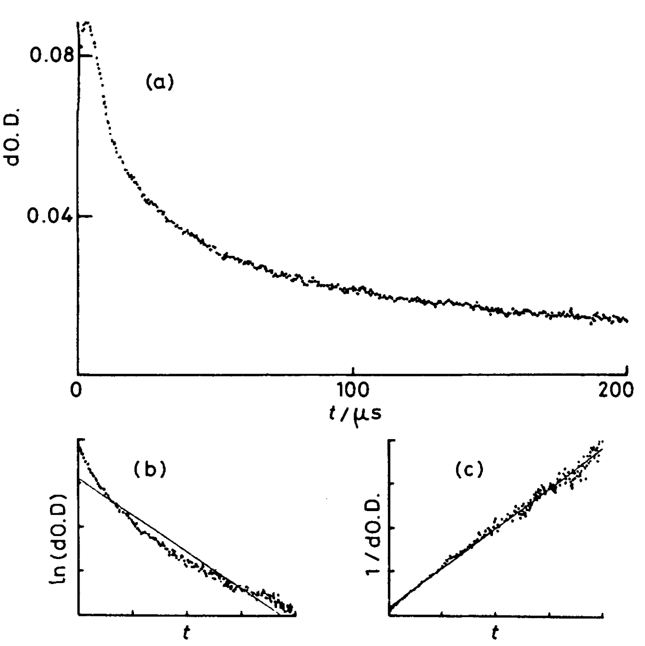

Figure 1. (a) Typical decay trace at 580 nm. (b), (c) Plots for first- and second-order kinetics, respectively (O.D. = optical density).

ligands and double-bond migration of 3-phenylpropene by the absorption of light.[7] On the other hand, the photoredox reaction associated with the hydrido ligand has been found not to take place, since the yields of molecular hydrogen, based on the complex, were only 1% when a cyclohexane or propan-2-ol solution of the complex (0.02 M) was irradiated by a 500 W high-pressure mercury lamp for 1 h *in vacuo*.

Cyclohexane solutions of $HCoL_4$ (1.6 mM) were deaerated by bubbling argon through, and then subjected to pulsed-laser photolysis at 337 nm, using a nitrogen laser. A typical decay trace monitored at 580 nm is shown in Figure 1(a). The application of first- and second-order kinetics to this trace led to the plots in Figure 1(b) and 1(c), respectively. Because the transient absorption clearly coincides with the plot corresponding to a second-order reaction, it is concluded that this transient corresponds not to any photoexcited states of $HCoL_4$, but to the co-ordinatively unsaturated species $HCoL_3$. The corresponding anionic complex $(CoL_4)^-$, which may be generated by the dissociation of the H ligand as a proton, cannot be the observed transient, since the potassium salt of an analogous complex is known to be colourless,[8] *i.e.* the anion has no absorption at 580 nm.

The differential absorption spectrum for the transient, observed 0.43 µs after the pulse, is shown in Figure 2. Since the relative intensities at each wavelength were constant to the end of the traces, a single species, namely $HCoL_3$, is responsible for the spectrum.

The addition of diethyl phenylphosphonite, L, or hex-1-ene to the solution shortened the life-time of the transient markedly, but differential spectra observed 0.43 µs after the pulse did not show any change in intensity and shape as compared with the case of the complex alone. It is therefore concluded that both the exchange of phosphorus ligands and the double-bond migration proceed *via* $HCoL_3$. The second-order rate constants for the co-ordination of diethyl phenylphosphonite, k_L, and hex-1-ene, k_h, to $HCoL_3$ have been estimated to be 1.4×10^8 and $1.1 \times 10^8\,dm^3\,mol^{-1}\,s^{-1}$, respectively, from pseudo-first-order rate constants. Although k_h is as large as k_L, the photochemical double-bond migration using $HCoL_4$ has been shown to be completely prevented by the addition of dialkyl phenylphosphonite.[7] This indicates that the rate-determining step of the double-bond migration corresponds to a later step than the co-ordination of an olefin, probably the insertion of an olefin into the hydrido–cobalt bond.

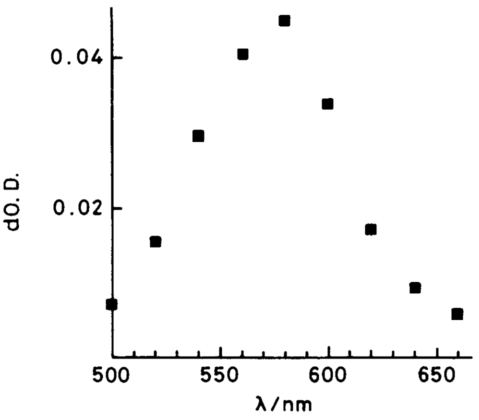

Figure 2. Differential absorption spectrum recorded 0.43 µs after pulse (O.D. = optical density).

The extinction coefficient, ε_{580} of $HCoL_3$ was estimated to be $1.7 \times 10^3\,dm^3\,mol^{-1}\,cm^{-1}$ from k_L/ε_{580} determined in the kinetics of Figure 1(c). The quantum yield for the generation of $HCoL_3$ was measured as 1.0 by a comparative method.[9] The extinction coefficient ε_{580} as determined by the ground state depletion method was almost the same as the value above.[10]

These results clearly support the idea that the photochemical excitation of $HCoL_4$ produces $HCoL_3$ which acts as an intermediate in both ligand exchange and double-bond migration. In the case of hydridocobalt complexes containing three phosphorus ligands and an easily dissociative ligand such as molecular nitrogen,[1,3—6] it is probable that co-ordinatively unsaturated species are generated thermally, and this is why these complexes show good catalytic activity.

The authors thank the Agency of Industrial Science and Technology of MITI under the Sunshine Project contract for support of part of this work.

Received, 20th January 1984; Com. 077

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