Mechanisms of Substitution Reactions of Platinum(0) Complexes

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Summary Some apparent anomalies relating to the substitution reactions of platinum(0) phosphine complexes have been resolved by demonstrating that such reactions proceed simultaneously through dissociative and associative pathways.

RECENT investigations on substitution reactions of platinum(0)–phosphine complexes such as $Pt(PPh_3)_3$, $Pt(PPh_3)_2$–(acetylene), and $Pt(PPh_3)_2(C_2H_4)$ have failed to give a satisfactory account of the mechanisms of these reactions.[1–5] While certain features of the kinetics could be interpreted in terms of dissociative mechanisms,[1–3] the resulting

interpretations were characterized both by internal inconsistencies[4] and by the need to assume dissociation equilibrium constants that were much larger than those derived from direct (*e.g.* n.m.r.) measurements.[1-3,5,7] From the results of the further investigations described here we conclude that both dissociative and associative pathways contribute significantly to the substitution reactions of platinum(0) complexes and that some of the earlier difficulties referred to above are due to failure to take account of the contribution from the latter pathway.

A clear demonstration of this behaviour is afforded by the results of an investigation of the equilibrium and kinetics of reaction (1) in benzene solution at 25 °C.

$$Pt(PPh_3)_3 + MeC{\equiv}CPh \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} Pt(PPh_3)_2(MeC{\equiv}CPh) + PPh_3 \quad (1)$$

The equilibrium constant of this reaction, determined both directly (from spectrophotometric measurements) as well as from rate measurements on both the forward and reverse reactions, was found to be 0·7. Thus, by appropriate adjustment of the concentrations of PPh_3 and $MeC{\equiv}CPh$ the kinetics of the reaction could readily be determined in both the forward and reverse directions. The kinetic measurements on the forward reaction encompassed the initial concentration ranges, *ca.* 1×10^{-4} M $Pt(PPh_3)_3$, 5×10^{-4} to 1×10^{-2} M PPh_3 and 2×10^{-2} to 3×10^{-1} M $MeC{\equiv}CPh$ and on the reverse reaction, 1×10^{-5} to 6×10^{-4} M $Pt(PPh_3)_2(MeC{\equiv}CPh)$, 0 to 2×10^{-2} M $MeC{\equiv}CPh$ and 1×10^{-3} to 6×10^{-1} M PPh_3. The ligand concentration ratios were adjusted so that in each experiment the reaction went to completion in the desired direction.

The results of the kinetic measurements clearly demonstrated the contributions of two simultaneous substitution pathways for the reaction in each direction, namely (i) the direct one-step *associative* pathway corresponding to equation (1), and (ii) the stepwise *dissociative* pathway described by equations (2) and (3).

$$Pt(PPh_3)_3 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} Pt(PPh_3)_2 + PPh_3 \quad (2)$$

$$Pt(PPh_3)_2 + MeC{\equiv}CPh \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} Pt(PPh_3)_2(MeC{\equiv}CPh) \quad (3)$$

Under conditions such that the equilibrium lies far to the right, the rate-law of the reaction is accordingly described by equation (4) which can readily be derived from the above mechanistic scheme by assuming the steady-state approximation for $Pt(PPh_3)_2$. An analogous rate-law can be deduced for the reverse reaction. Both rate-laws were found to fit the kinetic data accurately over the extensive concentration ranges described above yielding the following values for the rate constants, $k_1 = 5{\cdot}0 \times 10^{-2}$ l mol^{-1} s^{-1}, $k_2 = 0{\cdot}91$ s^{-1}, $k_{-2}/k_3 = 2{\cdot}5 \times 10^2$, $k_{-1} = 7{\cdot}1 \times 10^{-2}$ l mol^{-1} s^{-1}, $k_{-3} = 4{\cdot}5 \times 10^{-3}$ s^{-1}.

$$\text{Rate} = \left[k_1 + \frac{k_2k_3}{k_{-2}[PPh_3] + k_3[MeC{\equiv}CPh]}\right] [Pt(PPh_3)_3][MeC{\equiv}CPh] \quad (4)$$

Examination of the above rate-law and of the values of the rate constants reveals the following interesting and somewhat unusual feature of this reaction. Because of the differences in the ligand concentration ratios necessary to shift the equilibrium from the right to left and drive the reaction to completion in either direction, the forward reaction proceeds predominantly by the dissociative pathway, whereas the reverse reaction proceeds predominantly by the associative pathway. Thus, when the concentrations of PPh_3 and $MeC{\equiv}CPh$ are $1{\cdot}0 \times 10^{-3}$ and $3{\cdot}0 \times 10^{-1}$ M (1 : 300), respectively, the dissociative pathway accounts for 97% of the overall rate of the forward reaction. Conversely, when the concentrations of PPh_3 and $MeC{\equiv}CPh$ are $3{\cdot}0 \times 10^{-1}$ and $1{\cdot}0 \times 10^{-3}$, respectively (300 : 1) the associative pathway accounts for 80% of the overall rate of the reverse reaction. This calls attention to the caution that must be exercised in applying microscopic reversibility to infer the kinetics of a reaction in a given direction from a knowledge of the equilibrium constant combined with measurements of the kinetics in the opposite direction under different conditions.

The ease with which these platinum(0) complexes undergo substitution by dissociative as well as associative mechanisms implies that both the 14 and 18 valence-electron configurations are relatively stable and accessible for such d^{10} complexes of initial 16 electron configuration.

Support of this research through a grant from the National Science Foundation and through a Postdoctoral Fellowship (to T.A.W.) from the National Cancer Institute is acknowledged.

(*Received*, 11*th June* 1973; *Com.* 825.)

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