

Co(en)₃ and Co(sep) couples.

Likewise, from eq 14, the predicted change in reduction potential from the unstrained case is -0.029 V. The reduction potential of Co(sep) is 0.04 V less than that of Co(en)₃.

This crude calculation gives a fair rationalization of the cobalt sepulchrate redox properties. Presumably, better estimates of force constants using force field calculations could yield even better results.

This model may also be applicable to the study of metallo redox proteins. A protein, which can be viewed as a large ligand, could thus enormously affect the redox properties of its enclosed metal. Of course, the complications of deviation from simple geometry will be more pronounced with a protein than with a more symmetric cage ligand, and would require a more general force field analysis. The calculations in this paper hint at the significance of pocket size and ligand rigidity in determining redox properties.

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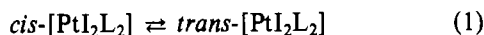
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Autocatalytic Isomerizations of Square-Planar Complexes

Sir:

We read with interest the note by Louw and van Eldik¹ describing the autocatalyzed isomerizations (1) (L = PEt₃ or PMe₂Ph)

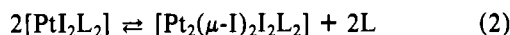


We would like to emphasize that this mechanism is probably quite common, and we have recently cited several likely examples.² To the best of our knowledge, the term "autocatalysis" was first applied to isomerizations of these types by ourselves in 1979.³

Perhaps the earliest reported reactions that may be classified in this category are those of Chatt and Wilkins in 1952.⁴ The

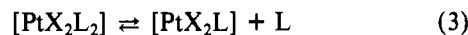
complexes [PtCl₂L₂] (L = AsEt₃ or SbEt₃) isomerize spontaneously, even in nonpolar solvents. When halide-bridged [Pt₂(μ-Cl)₂Cl₂(AsEt₃)₂] is added to the solutions to scavenge any free ligand, the isomerization reaction is either quenched (L = AsEt₃) or markedly slowed (L = SbEt₃). This is clearly analogous to the use, by Louw and van Eldik,¹ of [Ir(cod)(phen)]ClO₄ to scavenge catalyzing ligands. Other examples of autocatalysis have been cited elsewhere.²

Louw and van Eldik suggest¹ that loss of the catalyzing ligand L may be accompanied by halide-bridged dimer formation (eq 2), though its concentration in solution was never great enough for NMR detection.



The spontaneous isomerization of *trans*-[PtCl₂(CO)L] to its *cis* isomer, which probably also proceeds via autocatalysis involving CO loss,^{3,5} was accompanied by formation of 5–20% of [Pt₂(μ-Cl)₂Cl₂L₂]. In these examples, the catalyzing ligand, namely, CO, is gaseous and thus may be readily lost from solution, allowing a significant buildup of the dimeric species during the isomerization.

Finally, we have noted that the ligand elimination steps (2) or (3) can be either solvent-assisted or spontaneous,² though



it seems likely that even nonpolar solvents will associate with a three-coordinate platinum(II) intermediate. There now seems to be ample evidence that even nonpolar solvents such as benzene can cause elimination of ligands from platinum and palladium complexes in which the ligands are normally regarded as being strongly bonding, and the mechanistic consequences of such eliminations can be profound.² This latest example by Louw and van Eldik provides yet more evidence for the importance of solvents in reactions of square-planar complexes.

(5) Anderson, G. K.; Cross, R. J. *J. Chem. Soc., Dalton Trans.* 1980, 1988.

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(2) Anderson, G. K.; Cross, R. J. *Chem. Soc. Rev.* 1980, 9, 185.

(3) Anderson, G. K.; Cross, R. J. *Inorg. Chim. Acta* 1980, 44, L21.

(4) Chatt, J.; Wilkins, R. G. *J. Chem. Soc.* 1952, 4300.

Additions and Corrections

1981, Volume 20

A. Dedieu: Theoretical Study of the Olefin Insertion Step in the Chlorotris(triphenylphosphine)rhodium(I)-Catalyzed Hydrogenation of Olefins.

Page 2808. In Figure 6 one should read 11 instead of 13 and 12 instead of 16.—A. Dedieu