# Addition–Elimination Equilibrium between Three-Coordinate Pt(0) and Five-Coordinate Pt(II) Species

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The oxidative addition of an A–B species to a metal complex, and the reverse, reductive elimination, are key steps in many catalytic processes.[1] Several different mechanisms operate in these reactions[1] and studies of equilibria between oxidative addition and reductive elimination are of special importance in attempts to obtain more detailed mechanistic information. For d^{10} systems such equilibria have been observed for iridium(I)[2] but are rare for platinum (0).[3] A major reason appears to be fast consecutive reactions in the case of platinum, such as ligand dissociation,[4] insertion,[5] or alternative, competing reductive elimination reactions.[6] In previous work, we have shown that addition of halogen or alkyl halide to platinum(0) affords stable, 5-coordinate products according to Scheme 1.[7]

$$[Pt(N–N)(olefin)] + A–B \rightarrow [Pt(N–N)(olefin)(A)(B)]$$
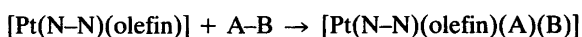
N–N is a bidentate nitrogen ligand such as 2,9-dimethyl-1,10-phenanthroline

Scheme 1.

The role of the steric and electronic effects of the ligands (both N–N and olefin) in stabilizing the 5-coordinate adducts against loss of olefin have been discussed elsewhere.[8] We have now extended our studies to the oxidative addition of halostannanes according to Scheme 2.[9] Here we report that reversible oxidative addition – reductive elimination is observed when the tin compound is $SnMe_2Cl_2$, the ligand 2,9-dimethyl-1,10-phenanthroline and the olefin
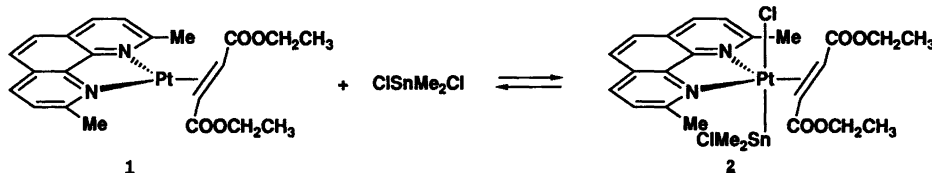
diethyl or dimethyl fumarate (Scheme 3). To the best of our knowledge, this is the first observation of an equilibrium involving 3-coordinate Pt(0) and 5-coordinate Pt(II).

$$[Pt(N–N)(olefin)] + Cl–SnR_{3-n}Cl_n \rightarrow$$

$$[Pt(N–N)(olefin)(Cl)(SnR_{3-n}Cl_n)]$$
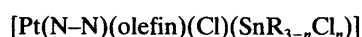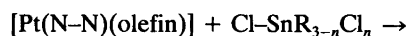
Scheme 2.

The 3-coordinate complex 1 was prepared from the corresponding ethene complex by exchange with diethyl fumarate in methanol solution.[7,10] The complex 1 was then converted into the 5-coordinate complex 2 by addition of 1.5 equivs. of $SnMe_2Cl_2$ to a solution of 1 in chloroform (15 mg ml^{-1}). The reaction was complete within a few seconds and the 5-coordinate complex 2 was isolated as white crystals by addition of diethyl ether.[11] The fact that a fresh solution of the complex in chloroform is non-conducting, strongly suggests that it is the 5-coordinate, non-ionic compound with the structure 2 rather than the alternative ion pair between chloride ion and a cationic 4-coordinate complex. It was observed by NMR spectroscopy that, in solution, the complex 2 partly reverted to the starting materials (Scheme 3).[12] From measurements at a number of different concentrations and temperatures it was established that the reaction is an equilibrium with the dissociation constant $K_{diss} = 10^{-3.2}$ and $\Delta H° = 11$ kcal mol^{-1} and $\Delta S° = 23$ cal mol^{-1} K^{-1}.

Scheme 3.

Preliminary data indicate that the properties of the R group of the (E)-ROOCCH=CHCOOR ligand (Me, Et, i-Pr, t-Bu) appear to affect strongly the position of the equilibrium leading to an increased preference for the 5-coordinate complex as the R-group becomes more bulky. Since reductive elimination generally requires a *cis* arrangement of the participating groups, it is notable that a facile equilibrium between oxidative addition and reductive elimination is established (Scheme 3) despite the *trans* configuration of 2. Further studies which include the influence of both neutral and ionic ligands are therefore in progress.

References

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10. ^{1}H NMR data [δ (ppm), J (Hz)]: 8.33 (d, 2 H), 7.75 (d, 2 H), 7.75 (s, 2 H), 4.11 (m, OCH_2), 3.80(81) (s, =CH), 3.25 (s, NCMe), 1.26 (t, CH_2Me).

11. Anal. Found: C, 36.3; H, 3.9; N, 3.5; $C_{24}H_{30}Cl_2N_2O_4PtSn$ Calc. C, 3625; H, 3.80; N, 3.52.

12. Selected ^{1}H NMR data for the five-coordinate complex: 3.40 (s, NCMe), 3.18 (s, NCMe), 0.88 (s, Sn–Me), 0.19 (s, Sn–Me).