Thermolysis of Complexes *cis*-[L_2PtAr_2]: Promotion of Reductive Elimination by Nucleophiles†

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Summary Pyrolysis of the title compounds gives Ar_2 quantitatively by a concerted intramolecular process and is promoted by excess of L; subsequent processes involve both P–C and C–H cleavage, but are not straightforward.

CURRENT interest[1] in reductive elimination as a pathway for transition-metal–carbon bond cleavage prompts us to report our findings (by T.G.A., D.T.A., D.S.C., and product analysis) on the condensed-phase pyrolyses of several species *cis*-[L_2PtAr_2] {Ar = Ph or 4-MeC_6H_4; L_2 = $(Ph_3P)_2$, $[(4\text{-}MeC_6H_4)_3P]_2$, $Ph_2PC_2H_4PPh_2$ (dppe), or $Ph_2PCH_2PPh_2$ (dppm)}. Thermolysis of the pure compounds under N_2 or argon at *ca.* 10 °C above the onset of decomposition gave rise to various aromatic products and red-brown residues, the natures of which have not been fully determined.

In all cases, the species Ar_2 is generated quantitatively‡ and without isomerisation. We take this to indicate concerted reductive elimination as the primary decom-

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† No reprints available.

‡ A marginal exception is [(dppm)Pt(4-MeC_6H_4)$_2$], which gives 16 mol% of toluene and 8 mol% of 4-methylbiphenyl, and only 89% of 4,4′-bitolyl.

position pathway. (Radical intermediates or primary *ortho*-metallation would both be expected to produce some ArH, while β-elimination to benzyne-metal hydrides would lead to isomerisation of the aryl). Contrary to an earlier report,[2] we find that secondary pyrolysis of the presumed L_2Pt is non-stoicheiometric, and gives rise to varying (but reproducible) amounts of RH and R_2, where R is an aryl originally bound to phosphorus. Pyrolysis of mixtures shows that whilst the primary elimination is purely intramolecular, the secondary process brings together aryl fragments originally in different molecules. Here, too, the failure of R in R_2 to isomerise restricts the range of possible pathways and the products found can be explained by competitive oxidative insertions of zerovalent metal into C–H and P–C bonds, followed by reductive elimination.

In order to test our view[3] that neutral nucleophiles can promote reductive elimination, we repeated the pyrolyses in the presence of added ligand ($L_2 : L_2PtAr_2 = 1:1$). In all cases the primary process was facilitated.§ Furthermore, secondary decompositions forming RH and R_2 are slower, as expected if the primary process now gives L_4Pt^0 or L_3Pt^0 rather than L_2Pt^0. When L_2 = dppe or dppm, however, either diphenylvinylphosphine or diphenylmethylphosphine is formed as an additional minor product. This can be explained by metal insertion into a CH_2–P bond, followed in the former case by β-elimination, but in the latter, perforce, by reductive elimination of Ph_2PCH_2 and hydride. Thus it appears that, in $(biL)_2Pt^0$, (biL = dppe or dppm) at least, platinum insertion occurs into alkyl–P, as well as aryl–P and C–H bonds.

$$\begin{tikzcd}
{[\mathrm{(dppe)PtPh_2}] + \mathrm{dppe}} \arrow[r, "480\ \mathrm{K}"] & {[\mathrm{(dppe)_2Pt}] + \mathrm{Ph_2}} \arrow[d, "590\ \mathrm{K}"] \\
 & {\mathrm{Ph_2(vinyl)P} + \mathrm{PhH} + \mathrm{Ph_2}}
\end{tikzcd}$$

Examples of nucleophilic promotion of reductive elimination {we regard the labilisation by alkenes of the metal–carbon bonds in $[(bipy)NiEt_2]$[4] as another example} are the more interesting in view of reports of phosphines inhibiting thermal decompositions in some cases. Phosphine inhibition in the thermal decomposition of *cis*-$[(Ph_3P)_2PtBu^n_2]$ is readily explained, since the primary process here is β-elimination.[5] The phosphine inhibition of reductive elimination from $[LAuR^1_2R^2]$ remains puzzling, however.[1a]

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§ This is not a trivial solution effect, since the use of (presumably) non-nucleophilic perhydrotriphenylene instead of phosphine failed to produce this effect.

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