Cationic Ruthenium Formyl Complexes, Evidence for a Homolytic Cleavage of the Ru–Formyl Bond in *trans*-[Ru(CHO)(CO)(dp)$_2$][SbF$_6$] [dp = 1,2-bis(diphenylphosphino)benzene]

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The complex, *trans*-[Ru(CHO)(CO)(dp)$_2$][SbF$_6$] [dp = 1,2-bis(diphenylphosphino)benzene] decomposes with first order kinetics to give *trans*-[RuH(CO)(dp)$_2$][SbF$_6$], *via* a free radical mechanism.

Metal formyl complexes are of interest because of their probable involvement as intermediates in the homogeneous hydrogenation of carbon monoxide and their decomposition reactions have received considerable attention.[1]

We have recently reported[2] that *trans*-[Ru(CHO)(CO)(dppe)$_2$][SbF$_6$] [dppe = 1,2-bis(diphenylphosphino)ethane] (**1**) decomposes by a mechanism involving cleavage of a Ru–P bond followed by rate-determining hydride migration and reco-ordination of the unbound phosphorus atom with expulsion of CO to give *cis*-[RuH(CO)(dppe)$_2$][SbF$_6$]. In a subsequent, slower step, this complex isomerises to the thermodynamically favoured *trans*-isomer.

In an attempt to prevent this decomposition pathway and prepare a more stable ruthenium formyl complex, we have synthesised *trans*-[Ru(CHO)(CO)(dp)$_2$][SbF$_6$] (**2**)† which contains the much more rigid [*o*-(Ph$_2$P)$_2$C$_6$H$_4$] ligand, by reaction of *trans*-[Ru(CO)$_2$(dp)$_2$][SbF$_6$]$_2$ with K[BH(OPr^i)$_3$] in CH_2Cl_2 at −30 °C.

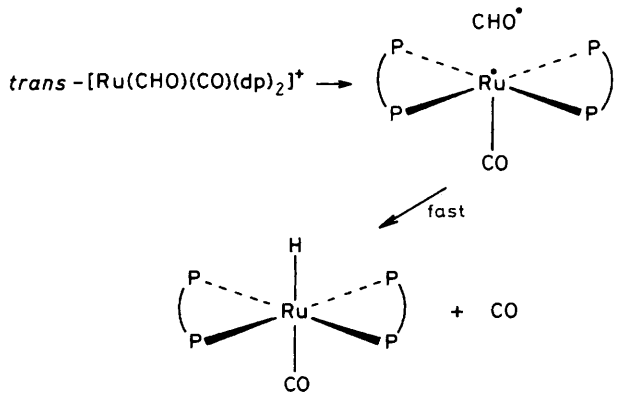
trans-[Ru(CHO)(CO)(P—P)$_2$][SbF$_6$]

(**1**) P—P = Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe)

(**2**) P—P = *o*-(Ph$_2$P)$_2$C$_6$H$_4$ (dp)

† I.r. $\nu_{max.}$/cm^{-1}: 1990s, ν(C≡O); 1603s, ν(C=O); 2558w, ν(C–H). N.m.r. (CD_2Cl_2) ^{1}H δ 11.5qn (J_{PH} 6 Hz); ^{31}P 56.6s p.p.m.

Complex (**2**) decomposes in CH_2Cl_2 at 30 °C with first order kinetics, but its decomposition differs from that of (**1**) in a number of important respects. Thus, (**2**) is less labile than (**1**), [$t_{\frac{1}{2}}$ 30.9 min, *cf.* 9.25 min for (**1**)] although a deuterium isotope effect of 2.4 is similar to that of (**1**) (1.8). More importantly, however, the only observable decomposition product is *trans*-[RuH(CO)(dp)$_2$][SbF$_6$], suggesting that concerted



Scheme 1. Mechanism of decomposition of *trans*-[Ru(CHO)(CO)(dp)$_2$]$^+$, P—P = dp.

hydride migration from the formyl ligand to the metal does not occur.

The most logical explanation of these observations is that (**2**) decomposes by homolytic cleavage of the Ru–C bond and that H$^{\bullet}$ is then transferred to the metal from [CHO]$^{\bullet}$.

This suggestion is confirmed by carrying out the decomposition of (**1**) and (**2**) in the presence of methyl methacrylate, which can undergo free radical initiated polymerisation at room temperature.[3] Compound (**2**) gives substantial quantities of poly(methyl methacrylate), whilst none is observed from the decomposition of (**1**).

Labelling studies involving co-decomposition of *trans*-[Ru(^{13}CHO)(^{13}CO)(dp)$_2$][SbF$_6$] and *trans*-[Ru(CDO)(CO)-(dp)$_2$][SbF$_6$] show that no crossover of the label occurs and hence that decomposition of [CHO]$^{\bullet}$ and attack of H$^{\bullet}$ on the ruthenium centre occur faster than escape from the solvent cage (see Scheme 1), although clearly one or other radical is sufficiently long-lived to arrive at the solvent cage and initiate polymerisation of methyl methacrylate.

Two other examples of free radicals being formed in the decomposition of formyl complexes have been reported,[4,5] but in both cases these reactions are photochemically initiated chain reactions or can be initiated by added radical initiators. Chain reactions of this kind should lead to crossover products from decomposition of mixed isotopically labelled molecules [not observed for (**2**)] and since (**2**) decomposes in the absence of light, we conclude that its decomposition represents the first reported example of thermal homolytic cleavage of a metal formyl bond.

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