

Ion Pairing Effects in the Formation of Ruthenium Formyls *via* Intermolecular Hydride Transfer

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For $M = K$, $M[\text{HRu}_3(\text{CO})_9(\text{dppe})]$ reacts with $\text{trans}[\text{Ru}(\text{CO})_2(\text{P-P})_2][\text{SbF}_6]_2$ [$\text{P-P} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$ (dppe) or $1,2\text{-bis}(\text{diphenylphosphino})\text{benzene}$ (dp)] to give $\text{trans}[\text{Ru}(\text{CHO})(\text{CO})(\text{P-P})_2]^+$ whereas for $M = \text{Na}$, no reaction is observed; the extent of ion-pairing is shown to be responsible for this difference in reactivity.

Details of the use of iodide promoters for the hydrogenation of carbon monoxide catalysed by $[\text{Ru}_3(\text{CO})_{12}]$ have recently appeared¹ and it has been proposed that the crucial formyl intermediate is formed by attack of hydride from $[\text{HRu}_3(\text{CO})_{11}]^-$ or $[\text{HRu}(\text{CO})_4]^-$ on a carbonyl of $[\text{Ru}(\text{CO})_3\text{I}_3]^-$ or a complex related to it such as $[\text{Ru}(\text{CO})_4\text{I}_2]$, and that the necessity for the use of polar aprotic (often chelating) solvents for successful CO reduction arises from the need to separate ion pairs which might otherwise form.^{1,2}

Direct evidence for these proposals comes from detailed kinetic and *in situ* i.r. studies¹ as well as from model studies in which it has been shown that $[\text{Re}(\text{C}_5\text{H}_5)(\text{NO})(\text{CO})(\text{CHO})]$ can be formed by reaction of $[\text{Re}(\text{C}_5\text{H}_5)(\text{NO})(\text{CO})_2]^+$ with $[\text{HRu}(\text{CO})_4]^-$. $[\text{HRu}_3(\text{CO})_{11}]^-$ does not act as a hydride donor to the same rhenium complex.^{1,3} Related studies have shown that $[\text{HRu}_3(\text{CO})_{11}]^-$ can act as a hydride donor to *e.g.* $[\text{B}(\text{OMe})_3]$ under CO and that the efficiency of hydride donation is reduced by ion-pairing with alkali metal cations.⁴ We now present direct evidence that hydride can be transferred from a cluster related to $[\text{HRu}_3(\text{CO})_{11}]^-$ onto a carbonyl group attached to another ruthenium atom and show that ion-pairing has a dramatic effect upon the efficiency of such reactions.

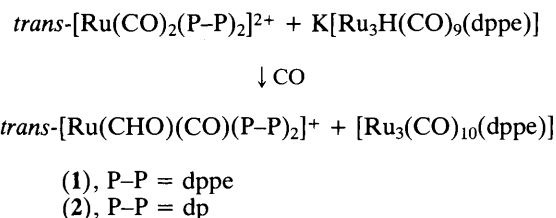
Reactions of $\text{trans}[\text{Ru}(\text{CO})_2(\text{P-P})_2][\text{SbF}_6]_2$ with $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ or $\text{PPN}[\text{HRu}(\text{CO})_4]$ [$\text{PPN} = \text{bis}(\text{triphenylphosphine})\text{iminium}$; $\text{P-P} = 1,2\text{-bis}(\text{diphenylphosphino})\text{ethane}$ (dppe) or $1,2\text{-bis}(\text{diphenylphosphino})\text{benzene}$ (dp)] in the presence or absence of CO give unidentified products, which are not the corresponding formyls,^{5,6} $\text{trans}[\text{Ru}(\text{CHO})(\text{CO})(\text{P-P})_2]^+$, nor any of their known decomposition products.^{6,7} In contrast, reaction of $\text{trans}[\text{Ru}(\text{CO})_2(\text{P-P})_2][\text{SbF}_6]_2$ with $\text{K}[\text{HRu}_3(\text{CO})_9(\text{dppe})]$ {which is a better hydride donor than $\text{K}[\text{HRu}_3(\text{CO})_{11}]$ on account of the higher electron density on the cluster},⁴ at -30°C in dichloromethane under carbon monoxide, leads to the formation‡ of $\text{trans}[\text{Ru}(\text{CO})(\text{CHO})(\text{P-P})_2]^+$ as the only observable mononuclear product (100% conversion in <10 min, ³¹P n.m.r. evidence). I.r. evidence shows that $[\text{Ru}_3(\text{CO})_{10}(\text{dppe})]$ is also formed (see Scheme 1). The formyls have been isolated from these reactions and have properties identical to those of authentic samples which have been characterised from reactions of $\text{trans}[\text{Ru}(\text{CO})_2(\text{P-P})_2][\text{SbF}_6]_2$ with borohydrides.^{5,6,8}

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‡ The exact mechanism of the reaction is not known although it may involve formation of intermediate MH .⁴ Since this may also occur in catalytic carbon monoxide reduction, the important conclusion is that inter-molecular hydride transfer can occur.

§ For (1): n.m.r. (CD_3NO_2 , -28°C) ¹H δ 13.52 (quintet, J_{PH} 8 Hz, CHO); ³¹P δ 46.9 (s) p.p.m.; i.r. (max, cm^{-1}) 1980s ($\nu_{\text{C=O}}$) and 1599s ($\nu_{\text{C-O}}$). For (2): n.m.r. (CD_3NO_2 , -28°C) ¹H δ 11.5 (quintet, J_{PH} 6 Hz, CHO); ³¹P δ 56.6 (s) p.p.m.; i.r. (max, cm^{-1}) 1990s ($\nu_{\text{C=O}}$) and 1602s ($\nu_{\text{C-O}}$).

As a means of probing possible cationic effects on such reduction reactions and hence obtaining insight into the role of different cations in the catalytic carbon monoxide hydrogenation reaction,¶ we have treated $\text{trans}[\text{Ru}(\text{CO})_2(\text{dp})_2][\text{SbF}_6]_2$ with $\text{Na}[\text{HRu}_3(\text{CO})_9(\text{dppe})]$ under conditions identical to those used for $\text{K}[\text{HRu}_3(\text{CO})_9(\text{dppe})]$ and find that no reaction occurs even after several hours (³¹P n.m.r. evidence). This observation prompted us to consider the effects of ion pairing, which are particularly likely to be identifiable in the non-coordinating CH_2Cl_2 solvent, since complexes of the type $\text{M}[\text{HM}'_3(\text{CO})_{11}]$ ($\text{M}' = \text{Fe}$ or Ru , $\text{M} = \text{Li}$, Na or K) are reported to form ion pairs in solution, with the order of stability of the ion pair being $\text{Li} > \text{Na} > \text{K}$.^{9,10} The following experiments were therefore performed. Firstly, $\text{Na}[\text{HRu}_3(\text{CO})_9(\text{dppe})]$ was treated with $\text{trans}[\text{Ru}(\text{CO})_2(\text{dp})_2][\text{SbF}_6]_2$ under identical conditions to those described above except that excess of dibenzo-18-crown-6 was added; $\text{trans}[\text{Ru}(\text{CHO})(\text{CO})(\text{dp})_2]^+$ was formed in quantitative yield. Secondly, $\text{K}[\text{HRu}_3(\text{CO})_9(\text{dppe})]$ was treated in the presence of excess of NaClO_4 , again under identical conditions to those described above, and production of the formyl complex was totally inhibited. These observations, which are summarised in Table 1, clearly show|| that it is the strength of the ion pair which accounts for the different reactivity of $\text{K}[\text{HRu}_3(\text{CO})_9(\text{dppe})]$ and $\text{Na}[\text{HRu}_3(\text{CO})_9(\text{dppe})]$.



Scheme 1. Reactions of $\text{trans}[\text{Ru}(\text{CO})_2(\text{P-P})_2]^{2+}$ with $\text{K}[\text{Ru}_3\text{H}(\text{CO})_9(\text{dppe})]$ under CO at -30°C in CH_2Cl_2 .

Table 1. The effect of different cations (M) and additives on the production of $\text{trans}[\text{Ru}(\text{CHO})(\text{CO})(\text{dp})_2]^+$ from $\text{trans}[\text{Ru}(\text{CO})_2(\text{dp})_2][\text{SbF}_6]_2$ and $\text{M}[\text{RuH}(\text{CO})_9(\text{dppe})]$.

M	Additive	% Yield of (2)
Na	—	0
K	—	100
Na	18-crown-6	100
K	NaClO_4	0

¶ In general, KI is a slightly better promoter than NaI for CO reduction catalysed by $[\text{Ru}_3(\text{CO})_{12}]^-$ even in highly co-ordinating solvents.^{1,8}

|| In both cases the reactions were totally homogeneous precluding the possibility that precipitation of a cation was occurring.

The isolation of formyl complexes from these reactions shows for the first time that formyl formation *via* intermolecular hydride transfer from one ruthenium complex to a carbon monoxide co-ordinated to a second ruthenium complex is possible and lends support to the suggestion that formyl formation *via* intermolecular hydride transfer may occur during the catalytic hydrogenation of carbon monoxide.¹ In addition, the fact that the formyl complex is formed from $[\text{HRu}_3(\text{CO})_9(\text{dppe})]^-$ but not from $[\text{HRu}_3(\text{CO})_{11}]^-$ suggests that subtle electronic changes may greatly affect the course of stoichiometric and, by extension, catalytic reductions of carbon monoxide.

Our results also confirm that the formation of ion pairs may well be important in determining the effect of different cationic promoters on the efficiency of carbon monoxide reduction in $[\text{Ru}_3(\text{CO})_{12}]/\text{I}^-$ catalysed reactions and show that disruption of the ion pairs by co-ordinating solvents may be crucial to the success of such reactions. It is interesting to note that 18-crown-6, which we have shown to be efficient for the disruption of ion-pairs of $\text{Na}\{\text{HRu}_3(\text{CO})_9(\text{dppe})_2\}$, appears to be a particularly suitable solvent for these catalytic reactions.^{1,8,11}

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