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Priority communication

Modelling intermediates in the catalytic carbonylation of CH_2I_2 to malonate esters; Evidence for a ketene pathway

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Abstract

From model intermediates and from labelling studies, a ketene-based mechanism is proposed for the double carbonylation of CH_2I_2 to malonate esters catalysed by $[RhX(CO)(PEt_3)_2]$ and for the deactivation of the catalyst. © 1998 Elsevier Science S.A.

Keywords: Catalytic carbonylation; Rhodium complexes; Labelling studies; Mechanism

Malonate esters are important intermediates in a variety of organic transformations and there are only a very few reports of their production from the catalytic carbonylation of dihaloalkanes. [1–7] We have recently reported that complexes of the form $[RhX(CO)(PEt_3)_2]$, (X = OAc, Cl or I) can catalyse the double carbonylation of CH_2I_2 as in Eq. (1) [8].

$$CH_2I_2 + CO \xrightarrow[EtOH]{[RhX(CO)(PEt_3)_2]} CH_2(CO_2Et)_2 \qquad (1)$$

The reaction only proceeds in low yield so we were interested to determine the mechanism in order to improve the process.

Our initial studies [9] showed that the oxidative addition of CH_2I_2 to $[RhCl(CO)(PEt_3)_2]$ proceeds smoothly to give $[RhCl(I)(CH_2I)(CO)(PEt_3)_2]$, which was structurally characterised, but that reaction of CO with this complex did not give the expected insertion product but rather $[RhX'_3(CO)(PEt_3)_2]$ (X'_3 is a mixture of Cl and I). Further attempts to produce an iodoacyl intermediate by oxidative addition of ICH_2COCl to $[RhCl(CO)(PEt_3)_2]$ also produced $[RhX'_3(CO)(PEt_3)_2]$, but diketene was detected as a product, suggesting that the iodoacyl complex may be unstable with respect to cleavage of the C–I bond and formation of an ionic ketene complex (Scheme 1).

We reasoned, therefore, that since the C–Cl bond is stronger than the C–I bond it might be possible to isolate an analogue of the putative iodoacyl intermediate from oxidative addition of $ClCH_2COCl$ to $[RhCl(CO)(PEt_3)_2]$. This reaction proceeds smoothly to give $[RhCl_2(COCH_2Cl)(CO)(PEt_3)_2]$ in high yield. This complex has the expected structure (see Fig. 1) with *trans*-phosphines and the chloroacyl group *trans* to Cl. We know of only one chloroacyl complex to have been structurally characterised [10], $[Co(COCH_2Cl)(CO)_3(PPh_3)]$, and, despite the rather low precision of our structure arising from disorder in the PEt_3 ligands, [1] the C–Cl bond in the rhodium complex does not appear to be especially weakened relative to that in the cobalt complex.

Assuming that the ketene complex does form from the iodoacyl species, it is possible to propose a new mechanism for the double carbonylation of CH_2I_2 (Scheme 2). This involves, in the last step, the reductive elimination of $ICOCCH_2COOEt$ from a rhodium (III) intermediate. We have modelled this intermediate by the oxidative addition of $ClCOCH_2COOEt$ to $[RhCl(CO)(PEt_3)_2]$ to form the monodentate ethylmalonyl complex, the structure of which is shown in

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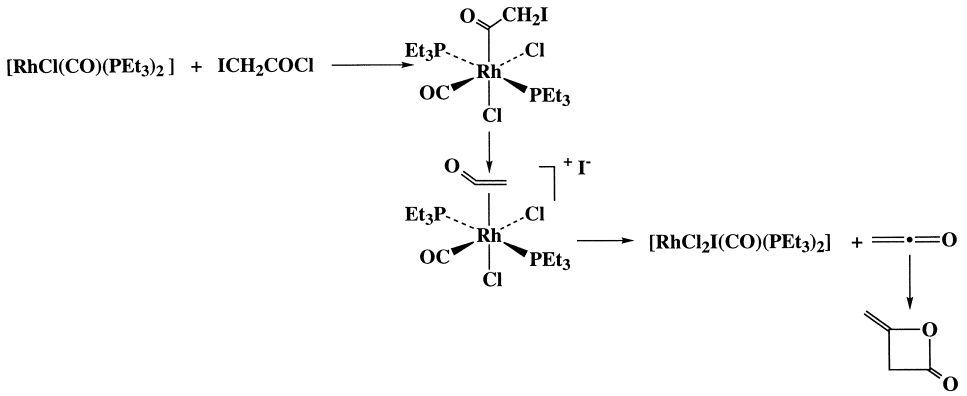
[1] Because the precision of the structure determinations is low, the data has not been deposited at the Cambridge Crystallographic Database, but full structural parameters are available from the authors.

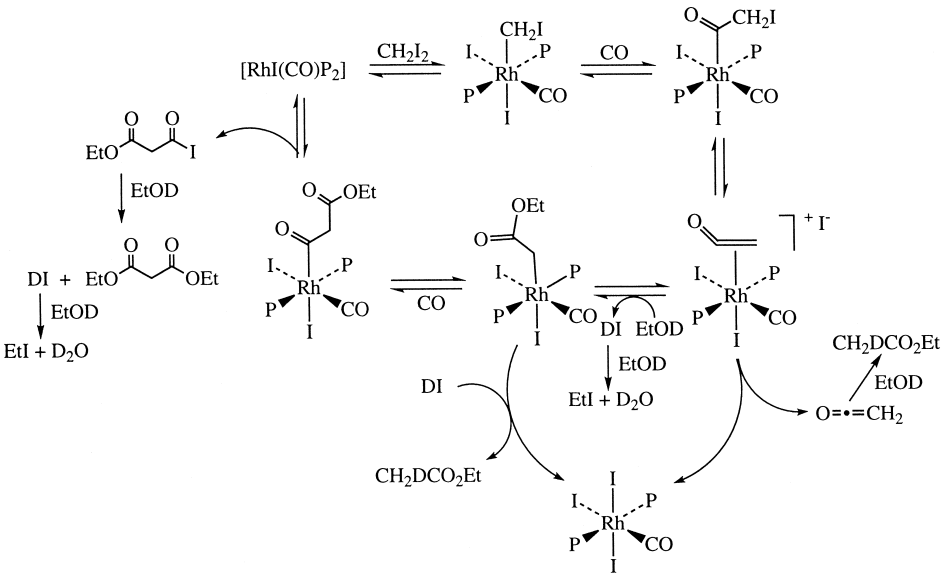


Scheme 1. Reaction between $[RhCl(CO)(PEt_3)_2]$ and ICH_2COI in CH_2Cl_2.

Fig. 2. Once again unresolved disorder in the PEt_3 ligands means that only the major structural features are reliable. [1] The structure of $[RhCl_2(COCH_2CO_2Et)(CO)(PEt_3)_2]$ is similar to that of $[RhCl_2(COCH_2Cl)(CO)(PEt_3)_2]$ but has the CO_2Et group replacing the Cl atom on the chloroacyl ligand. Refluxing $[RhCl_2(COCH_2CO_2Et)(CO)(PEt_3)_2]$ in ethanol produces $[RhCl(CO)(PEt_3)_2]$ and diethylmalonate, thus modelling the last step of the proposed mechanism.

Studies on catalytic solutions after formation of diethylmalonate show that the major rhodium containing species present is $[RhI_3(CO)(PEt_3)_2]$ and that this is not catalytically active. This suggests that the poisoning of the catalyst may occur by displacement of ketene from the ketene complex by I^-. To confirm this, we have carried out catalytic reactions using preformed $[RhI(CO)(PEt_3)_2]$ and MeI free CH_2I_2 (to prevent formation of EtOAc from MeI) [11]. In these reactions, EtOAc is observed as a product, the amount being approximately equivalent to one mole per mole of catalyst. That this arises from ketene has been confirmed by carrying out the reaction in EtOD and showing that only CH_2DCO_2Et is formed. This labelling pattern can only be explained by addition of EtOD to ketene. Ketenes have only rarely been proposed as intermediates in carbonylation reactions [12–14], but one example is $[Co_2(CO)_7(CH_2=C=O)]$ isolated as an intermediate in the cobalt catalysed carbonylation of CH_2Br_2 to malonate esters [12].

We believe that the mechanism of Scheme 2 offers a plausible explanation for the double carbonylation of



Scheme 2. Proposed mechanism for the double carbonylation of CH_2I_2 to malonic acid esters catalysed by $[RhI(CO)(PEt_3)_2]$ and for the deactivation of the catalyst. P = PEt_3.

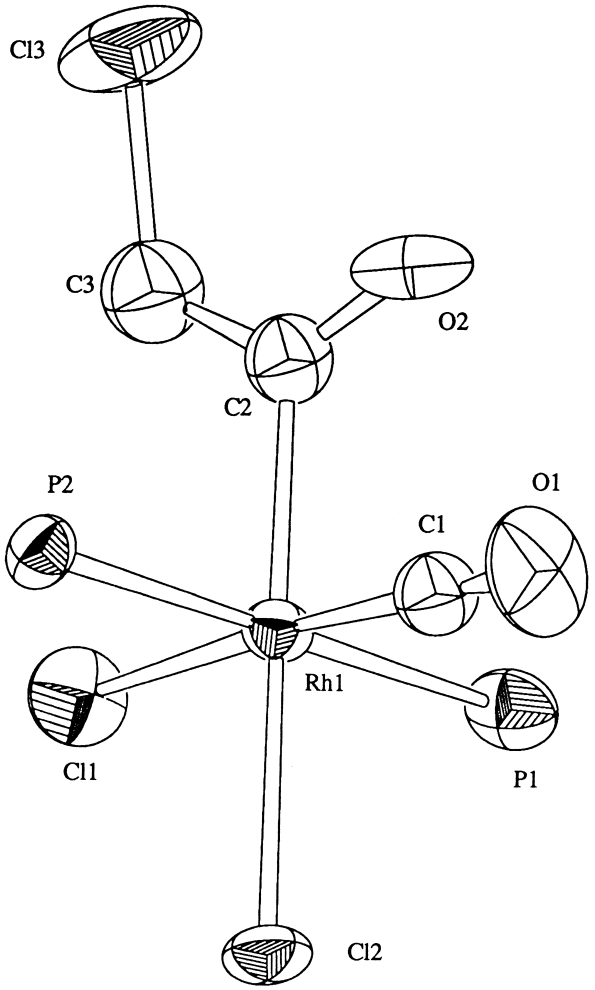


Fig. 1. X-ray structure and numbering scheme for $[RhCl_2(COCH_2Cl)(CO)(PEt_3)_2]$ $M = 515.63$, $p1$, $a = 13.048(8)$, $b = 15.169(5)$, $c = 11.994(8)$ Å; $\alpha = 95.89(4)$, $\beta = 95.16(6)$, $g = 103.09(4)°$; $V = 2284(2)$ Å^3, $Z = 4$, $D = 1.50$ g cm^{-3}; $R = 0.164$. Rh(1)–C(2) 2.06(3), C(2)–C(3) 1.48(4), C(2)–O(2) 1.20(3), C(3)–Cl(3) 1.80(3) Å, Rh(1)–C(2)–O(2) 121(2), Rh(1)–C(2)–C(3) 116(2), O(2)–C(2)–C(3) 121(2), C(2)–C(3)–Cl(3) 111°. H atoms and ethyl groups, which show significant disorder, have been omitted for clarity.

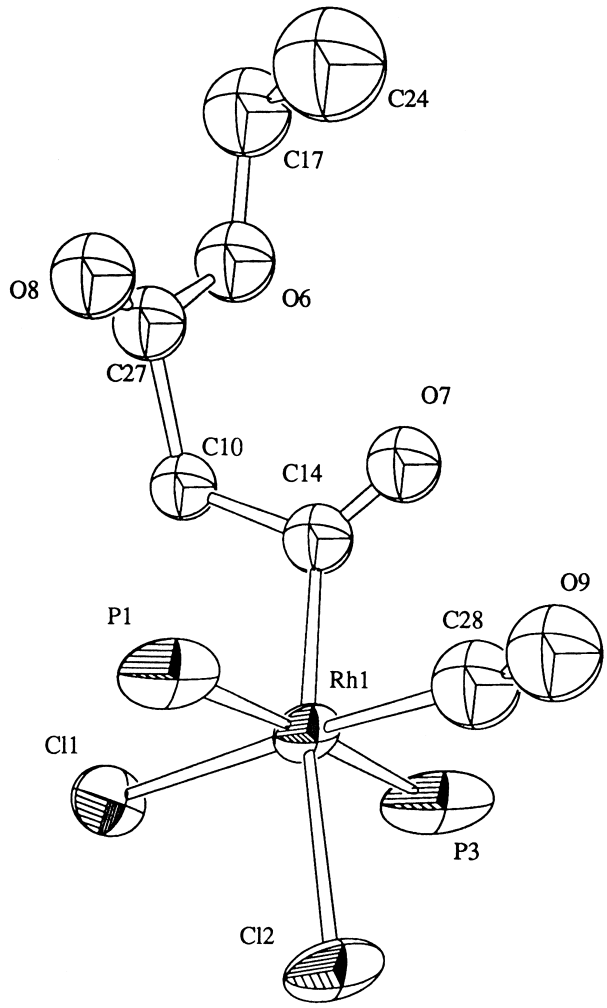


Fig. 2. X-ray structure and numbering scheme for $[RhCl_2(COCH_2CO_2Et)(CO)(PEt_3)_2]$. $M = 553.25$, $p1$, $a = 11.909(5)$, $b = 11.967(3)$, $c = 9.254(3)$ Å; $\alpha = 105.47(2)$, $\beta = 95.22(3)$, $\gamma = 91.36(3)°$; $V = 1264.2(7)$ Å^3, $Z = 2$, $D_x = 1.45$ g cm^{-3}; $R = 0.191$. Rh(1)–C(14) 2.05(4), C(14)–O(7) 1.1(4), C(14)–C(10) 1.57(5), C(10)–C(27) 1.61(5), C(27)–O(8) 0.96(5), C(27)–O(6) 1.35(5), O(6)–C(14) 1.44(5) Å; Rh(1)–C(14)–O(7) 126(3), Rh(1)–C(14)–C(10) 115(2), O(7)–C(14)–C(10) 117(3), C(14)–C(10)–C(27) 113(3), C(10)–C(27)–O(8) 113(5), C(10)–C(27)–O(6) 101(3), O(6)–C(27)–O(8) 125(4), C(27)–O(6)–C(17) 121°. H atoms and ethyl groups on phosphorus, which show significant disorder, have been omitted for clarity.

CH_2I_2 catalysed by $[RhI(CO)(PEt_3)_2]$ and for the poisoning of the catalyst. [2] There are a number of different possible routes from the ketene complex to the ethylmalonyl complex. We favour nucleophilic attack of ethoxide on the carbonyl C atom of the ketene followed by CO insertion into the Rh–C bond because ketene is highly reactive towards nucleophiles and this reactivity is likely to be further enhanced by coordination to a cationic rhodium centre. Direct competition between protonation of the bound $Rh(CH_2CO_2Et)$ ligand and CO insertion would account for the observed linear increase in the yield of diethylmalonate as p_{CO} is increased.

[2] In our previous report [8], we tentatively proposed a binuclear mechanism involving a bridging carbene for the catalytic reaction. However, attempts to form such a complex by reaction of $[Rh(CH_2I)ICl(CO)(PEt_3)_2]$ with $[RhCl(CO)(PEt_3)_2]$ were unsuccessful, so we do not believe that the mechanism operates.

Acknowledgements

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