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Preliminary communication

THE MECHANISM OF THE ADDITION OF TETRACHLOROMETHANE TO OCT-1-ENE CATALYSED BY $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$

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Summary

A study of the reaction of CCl_4 with oct-1-ene in the presence of catalytic amounts of $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ has shown that in the early stages it proceeds by a redox-catalysed mechanism. However, gradual decomposition of the catalyst leads to the intervention of a radical chain pathway.

The recent paper by Poë and coworkers [1] concerning the homolytic fission of the metal—metal bond in $[Mo_2(CO)_6(\eta\text{-}Cp)_2]$ (I) and subsequent reactions of the $[Mo(CO)_3(\eta\text{-}Cp)^\bullet]$ radical so formed prompts us to report our studies of the use of I as a catalyst for the addition of tetrachloromethane to oct-1-ene. This reaction was first described by Susuki and Tsuji [2] as part of a study of the reactions between alkenes and CCl_4, in both the presence and absence of carbon monoxide, catalysed by I, $[Fe_2(CO)_4(\eta\text{-}Cp)_2]$ and $[Co_2(CO)_8]$. These authors suggest such reactions proceed by the mechanism shown in eq. 1—3; however, two alternative mechanisms have to be considered. These are, (a) the radical chain mechanism of Karasch (eq. 4—6) [3] and (b) a redox catalysed route similar to that observed for reactions catalysed by

$$I + CCl_4 \rightarrow [MoCl(CO)_3(\eta\text{-}Cp)] + [Mo(CCl_3)(CO)_3(\eta\text{-}Cp)] \qquad (1)$$

$$[Mo(CCl_3)(CO)_3(\eta\text{-}Cp)] + RCH{=}CH_2 \rightarrow [Mo(CHRCH_2CCl_3)(CO)_3(\eta\text{-}Cp)] \qquad (2)$$

$$[Mo(CHRCH_2CCl_3)(CO)_3(\eta\text{-}Cp)] + CCl_4 \rightarrow RCHClCH_2CCl_3 + [Mo(CCl_3)(CO)_3(\eta\text{-}Cp)] \qquad (3)$$

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$$\mathrm{I + CCl_4 \rightarrow [MoCl(CO)_3(\eta\text{-}Cp)] + CCl_3\cdot} \tag{4}$$

$$\mathrm{RCH{=}CH_2 + CCl_3\cdot \rightarrow R\dot{C}HCH_2CCl_3} \tag{5}$$

$$\mathrm{R\dot{C}HCH_2CCl_3 + CCl_4 \rightarrow RCHClCH_2CCl_3 + CCl_3\cdot} \tag{6}$$

chlorides or iron and copper [4a] and $Fe(CO)_5$ [4b] (eq. 7—10). The evidence for the mechanism shown in eq. 1—3 rested principally upon the lack of inhibition by hydroquinone. Our previous interests in the chemistry of organo-transition metal centred free radicals [5] led us to examine the title reaction in detail, and we have found that satisfactory yields can be obtained under milder conditions than those reported previously [2]. Thus, a preparative reaction between CCl_4 and oct-1-ene in the presence of I gave ca. 60% of the 1/1 addition product after refluxing for 2 h at 80°C.

$$\mathrm{I + CCl_4 \rightarrow [MoCl(CO)_3(\eta\text{-}Cp)] + CCl_3\cdot + [Mo(CO)_3(\eta\text{-}Cp)\cdot]} \tag{7}$$

$$\mathrm{CCl_3\cdot + RCH{=}CH_2 \rightarrow R\dot{C}HCH_2CCl_3} \tag{8}$$

$$\mathrm{R\dot{C}HCH_2CCl_3 + [MoCl(CO)_3(\eta\text{-}Cp)] \rightarrow RCHClCH_2CCl_3 + [Mo(CO)_3(\eta\text{-}Cp)\cdot]} \tag{9}$$

$$\mathrm{2[Mo(CO)_3(\eta\text{-}Cp)\cdot] \rightarrow I} \tag{10}$$

A kinetic study of the reaction employing the initial rate method showed the rate to have a first order dependence on both I and CCl_4, while it is independent of alkene concentration. This is clearly inconsistent with the radical chain mechanism which follows the rate law:

$$\mathrm{Rate} \propto [\mathrm{I}]^{1/2}[\mathrm{CCl_4}]^{1/2}[\mathrm{alkene}]$$

It does not, however, differentiate between the mechanisms shown in eq. 1—3 and 7—10. After approximately fifteen minutes there is increasing deviation from the kinetic orders given above. For example, the order with respect to CCl_4 decreases from unity.

Relevant to this finding are the following observations: (i) there is no infrared evidence for I at the end of the reaction, neither are there any other CO stretching bands, indicating the absence of any metal carbonyl-containing species; (ii) the yield of $C_6H_{11}CHClCH_2CCl_3$ increases even after the disappearance of all metal carbonyl species as evidenced by monitoring the reaction by GLC and IR spectroscopy; (iii) although I reacts with CCl_4 in a separate reaction to give $[MoCl(CO)_3(\eta\text{-}Cp)]$, this rapidly decomposes under the reaction conditions. On the basis of these observations, we believe that as the metal carbonyl containing species are decomposed, the reaction continues by a free radical chain route in which chains are initiated by the metal-containing decomposition products.

The distinction between eq. 1—3 and 7—10 depends on the observation of the intermediate $[Mo(CCl_3)(CO)_3(\eta\text{-}Cp)]$ (II). In the early stages of the reaction there is no IR evidence for any carbonyl containing species other than I and $[MoCl(CO)_3(\eta\text{-}Cp)]$ (III). This does not, however, preclude the transient existence of II or the chance coincidence of the IR bands of II and bands from I and III. II has not been previously reported and it is noteworthy that well-characterised examples of trichloromethylmetal complexes are scarce [6].

The reaction of oct-1-ene with $n\text{-}C_3F_7I$ in the presence of $CuCl_2$-ethanolamine has been reported [7] to yield $C_6H_{11}CHICH_2C_3F_7$ and a similar reaction performed in this work in the presence of I gave this compound in good yield. If this reaction proceeds via the route shown in eq. 1—3, the complex $[Mo(C_3F_7)(CO)_3(\eta\text{-}Cp)]$ (IV) should be formed. In order to check the CO stretching frequencies of IV under the conditions of the addition reaction, it was prepared by the previously reported method [8]. Furthermore, when IV was refluxed under the reaction conditions, its IR spectrum remained unchanged over several hours. The reaction between $n\text{-}C_3F_7I$ and oct-1-ene in the presence of I was monitored by IR spectroscopy and showed no evidence for the formation of IV. These results, therefore, favour the mechanism shown in eq. 7—10.

The stoichiometry of the initiation step was also studied in order to distinguish between step 7 and the alternative reaction 11. Quantitative IR data for the formation of $[MoI(CO)_3(\eta\text{-}Cp)]$ (V) in the addition of C_3F_7I to oct-1-ene showed one equivalent of V to be formed from I, $[Mo(CO)_3(\eta\text{-}Cp)\cdot]$ presumably being the other metal-containing product (this reaction was chosen in preference to CCl_4 addition, as V is stable under the reaction conditions, whereas III undergoes slow decomposition and thus V can be quantified at the end of the reaction). Poë et al. suggest similar, although more complex, behaviour of I in the presence of $C_{16}H_{33}I$ [1].

$$I + 2CCl_4 \rightarrow 2[MoCl(CO)_3(\eta\text{-}Cp)] + 2CCl_3\cdot \qquad (11)$$

Finally, it is noteworthy that step 1 involves an oxidative addition across a metal—metal bond, a reaction similar to that between I and I_2 [9]. In the latter reaction, good evidence has been obtained for an ionic route involving the intermediate $[(\eta\text{-}Cp)(OC)_3Mo(\mu\text{-}I)Mo(CO)_3(\eta\text{-}Cp)]^+ I^-$. Such an ionic mechanism is unlikely to be followed with CCl_4.

In summary, we believe these addition reactions initially follow a redox-catalysed mechanism, but this is gradually replaced by a radical chain process as the metal carbonyl species decompose. This initial route, involving a one-electron oxidation-reduction cycle of the metal, contrasts with the more usual two-electron (oxidative addition-reductive elimination) cycle observed for other alkene addition reactions.

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