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Preliminary communication

HALOGENATION OF BIS(η -CYCLOPENTADIENYLTRICARBONYLMOLYBDENUM AND -TUNGSTEN) VIA BRIDGED INTERMEDIATES — FORMATION OF SOME MONOCYCLOPENTADIENYL DERIVATIVES OF MOLYBDENUM(IV)

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Summary

The synthesis of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{LI}]$ ($\text{L} = \text{CO}$ or $\text{P}(\text{OCH}_3)_3$) and $[\text{W}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{I}]$ by iodination of $[\{\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}\}_2]$ and $[\{\text{W}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\}_2]$, respectively, is shown to proceed via iodide bridged intermediates, $[\{\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{L}\}_2\text{I}]^+$ ($\text{M} = \text{Mo}$ or W); treatment of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{LX}]$ $\{\text{X} = \text{Cl}, \text{Br}$ or $\text{I}; \text{L} = \text{CO}, \text{P}(\text{C}_2\text{H}_5)_3, \text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$ or $\text{P}(\text{OCH}_3)_3; \text{L} \neq \text{P}(\text{C}_6\text{H}_5)_3\}$ with excess halogen leads to the formation of the molybdenum(IV) derivatives, $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{LX}_3]$.

Previous studies on the halogenation reactions of the dinuclear metal carbonyl derivatives, $[\{\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\}_2]$ ($\text{M} = \text{Fe}$ or Ru), $[\{\text{Fe}(\text{CO})_3\text{SR}\}_2]$ ($\text{R} = \text{alkyl}$ or aryl group) and substituted derivatives of the latter have indicated that they proceed via halide bridged intermediates [1–5]. All of the above compounds contain either bridging carbonyl or bridging thiol groups [6–13]. With a view to establishing whether such a mechanism would operate for non-bridged species the halogenation of $[\{\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\}_2]$ ($\text{M} = \text{Mo}$ or W) [14, 15] has been investigated.

By monitoring the reaction of these compounds with iodine in dichloromethane by means of infrared spectroscopy intermediates in the formation of $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{I}]$ could be detected. Their presence was shortlived however and their C—O stretching modes were observed to decrease in intensity with increase in intensity of the peaks corresponding to $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{I}]$; the de-

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crease was rapid for $M = Mo$ but occurred at a more moderate rate for $M = W$. These species could nevertheless be isolated by performing the iodinations in the presence of $Na[B(C_6H_5)_4]$ in either ethanol at $0^\circ C$ or toluene, plus sufficient ethanol to effect the dissolution of the counterion, at $-15^\circ C$. The compounds which separated from solution were characterised as the iodide bridged derivatives $[\{M(\eta-C_5H_5)(CO)_3\}_2 I] [B(C_6H_5)_4]$.

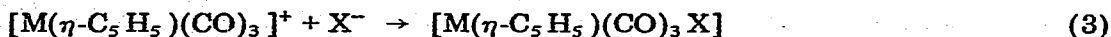
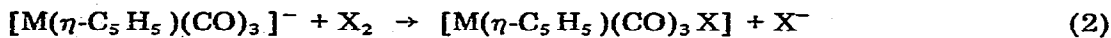
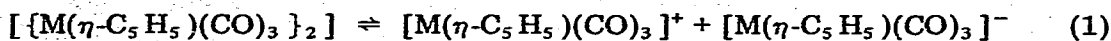
Bromination of $[\{M(\eta-C_5H_5)(CO)_3\}_2]$ in dichloromethane was found to lead to the rapid formation of $[M(\eta-C_5H_5)(CO)_2Br_3]$ [16, 17] via $[M(\eta-C_5H_5)(CO)_3Br]$, irrespective of the $Br_2 / [\{M(\eta-C_5H_5)(CO)_3\}_2]$ molar ratio employed. $[\{M(\eta-C_5H_5)(CO)_3\}_2 Br]^+$ could not be detected in this reaction nor for that matter could it be isolated by performing the bromination in ethanol in the presence of a counterion but this is attributed to the rapid rate of formation of the two neutral products. The chlorination reactions of $[\{M(\eta-C_5H_5)(CO)_3\}_2]$ were found to be even more rapid than the corresponding brominations such that the neutral chloride $[M(\eta-C_5H_5)(CO)_3Cl]$ became difficult to detect in the formation of $[Mo(\eta-C_5H_5)(CO)_2Cl_3]$.

The reaction of the substituted derivative $[\{Mo(\eta-C_5H_5)(CO)_2P(OCH_3)_3\}_2]$ [18] with iodine was also studied and, as for the corresponding reactions involving the unsubstituted compounds, $[\{M(\eta-C_5H_5)(CO)_3\}_2]$, an ionic species viz. $[\{Mo(\eta-C_5H_5)(CO)_2P(OCH_3)_3\}_2 I]^+$, was found to be an intermediate in the formation of the neutral product, $[Mo(\eta-C_5H_5)(CO)_2P(OCH_3)_3I]$.

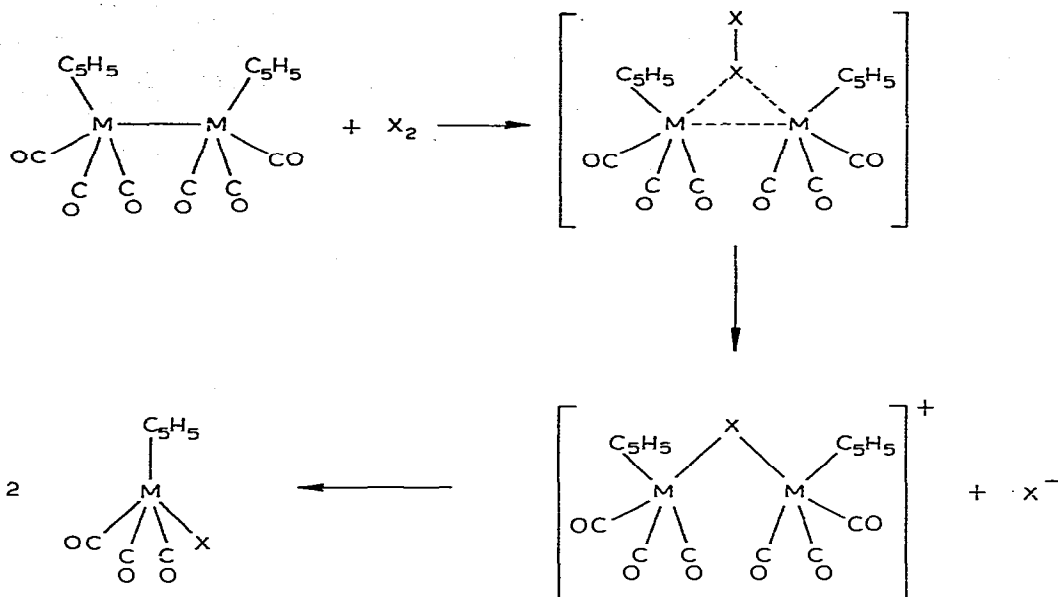
$[\{M(\eta-C_5H_5)(CO)_3\}_2 I]^+$ ($M = Mo$ or W) were observed to react very readily with iodide ions to produce $[M(\eta-C_5H_5)(CO)_3I]$, consistent with these species being intermediates in the formation of the latter from $[\{M(\eta-C_5H_5)(CO)_3\}_2]$. These cationic derivatives are also susceptible to attack by neutral nucleophiles and $[\{Mo(\eta-C_5H_5)(CO)_3\}_2 I]^+$ for instance reacts readily with acetone, pyridine, $P(C_6H_5)_3$ and $P(OCH_3)_3$ to afford $[Mo(\eta-C_5H_5)(CO)_3(Nu)]^+$ ($Nu =$ nucleophile) and $[Mo(\eta-C_5H_5)(CO)_3I]$.

On the basis of the above results it is suggested that halogenation of $[\{M(\eta-C_5H_5)(CO)_3\}_2]$ ($M = Mo$ or W) occurs by the mechanism proposed for $[\{M'(\eta-C_5H_5)(CO)_2\}_2]$ ($M' = Fe$ or Ru) and $[\{Fe(CO)_3SR\}_2]$ ($R =$ alkyl or aryl group) [1-5]. This involves (i) electrophilic attack of the halogen molecule on the metal complex resulting in heterolytic cleavage of the halogen-halogen bond and the formation of the halide bridged cationic intermediate through a three-centre transition state, and (ii) subsequent nucleophilic attack of the halide ion on the intermediate to give the neutral halide as shown in Scheme 1.

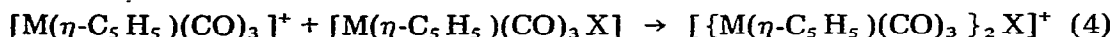
Although $[M(\eta-C_5H_5)(CO)_3]$ ($M = Mo$ or W) [19-21] radicals can be readily generated under photochemical conditions*, a radical mechanism is eliminated on the basis that it cannot readily explain the formation of $[\{M(\eta-C_5H_5)(CO)_3\}_2 X]^+$. A further possibility involving the heterolytic fission of $[\{M(\eta-C_5H_5)(CO)_3\}_2]$ according to equations 1-4.



*These radicals react readily with chlorocarbon trapping agents to produce $[M(\eta-C_5H_5)(CO)_3Cl]$ [21].



SCHEME 1



$[\{\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\}_2\text{X}]^+ + \text{X}^- \rightarrow 2[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{X}]$ is discarded on the basis that only $[\{\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\}_2\text{I}]^+$ ($\text{M} = \text{Mo}$ or W) was observed to be formed in the initial stages of the iodination of $[\{\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\}_2]$.

Similar to that established previously for $[\text{M}(\eta\text{-C}_5\text{H}_5)(\text{CO})_3\text{X}]$ ($\text{M} = \text{Mo}$ or W ; $\text{X} = \text{Cl}$, Br or I) [16, 17], the substituted derivatives $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{LX}]$ ($\text{X} = \text{Cl}$, Br or I ; $\text{L} = \text{P}(\text{OCH}_3)_3$, $\text{P}(\text{C}_2\text{H}_5)_3$ or $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$) react readily with halogens to produce molybdenum(IV) compounds of the type $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{LX}_3]$. $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{P}(\text{C}_6\text{H}_5)_3\text{X}]$ on the other hand affords $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2\text{X}_3]$ on attack by halogens. This difference in behaviour can be attributed to the greater steric bulk of the triphenylphosphine ligand [22]. A similar explanation will account for the instability of $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})\text{LI}_3]$ ($\text{L} = \text{P}(\text{C}_2\text{H}_5)_3$ or $\text{P}(\text{CH}_3)_2\text{C}_6\text{H}_5$) in solution.

Acknowledgements

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