

Preliminary communication

THE TRANSITION METAL CATALYSED REACTION BETWEEN $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{I}$ AND ISONITRILES

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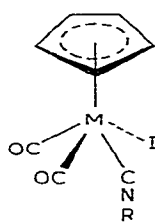
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Summary

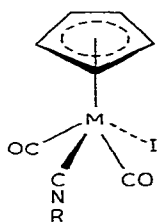
The reaction between $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{I}$ and RNC is catalysed by $[\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3]_2$ and readily yields $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_{3-n}(\text{RNC})_n\text{I}$ ($n = 1-3$). A free radical mechanism is consistent with the experimental data.

The use of transition metals as catalysts in preparative organometallic chemistry has not been fully exploited [1,2]. In a continuation of our own studies in this area [2] we have commenced an investigation of the use of transition metals as catalysts to bring about substitution reactions on organometallic complexes which, under moderate thermal conditions, occur with difficulty. Herein, we report on the preparation of $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_{3-n}(\text{RNC})_n\text{I}$ ($n = 1-3$) complexes from $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3\text{I}$ (I) and RNC using $[\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_3]_2$ (II) as catalyst.

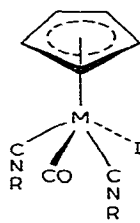
Addition of one or two equivalents of RNC [$\text{R} = \text{C}_6\text{H}_5\text{CH}_2$; $(\text{CH}_3)_3\text{C}$; 2,6- $(\text{CH}_3)_2\text{-C}_6\text{H}_3$] (1 or 2 mmol) to a refluxing benzene solution of I (1 mmol) and II (0.02 mmol) readily (< 30 min) leads to either $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}_2(\text{RNC})\text{I}$ (III) or $\eta^5\text{-C}_5\text{H}_5\text{Mo(CO)}(\text{RNC})_2\text{I}$ (IV) in yields between 50–85%. In the absence of dimer the reactions are slow and yields poor to non-existent even after extended reaction times [3–5]. The new products were characterized by elemental analyses, NMR and IR (Table 1). In all cases these complexes exist as a mixture of isomers IIIa and IIIb or IVa and IVb.



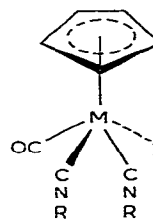
(III a)



(III b)



(IV a)



(IV b)

TABLE 1

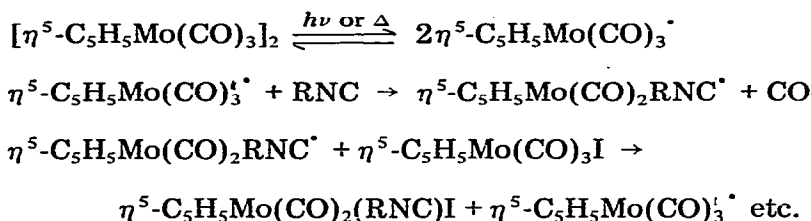
IR DATA FOR THE ISONITRILE COMPLEXES^a

	$\nu(\text{NC}) (\text{cm}^{-1})$	$\nu(\text{CO}) (\text{cm}^{-1})$
$\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[(\text{CH}_3)_3\text{CNC}]\text{I}$	2138	1973 1915 1902
$\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}]\text{I}$	2115	1977 1924 1912
$\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2[\text{C}_6\text{H}_5\text{CH}_2\text{NC}]\text{I}$	2156	1978 1913
$\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_2[(\text{CH}_3)_3\text{CNC}]\text{I}$	2127	1962 1902 1889
$\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[(\text{CH}_3)_3\text{CNC}]\text{I}$	2132 2100 2062	1891 1866
$\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}]\text{I}$	2106 2066 1996	1905 1895
$\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})[\text{C}_6\text{H}_5\text{CH}_2\text{NC}]\text{I}$	2114	1894 1878
$\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})[(\text{CH}_3)_3\text{CNC}]\text{I}$	2087 2067	1882 1857
$\eta^5\text{-C}_5\text{H}_5\text{Mo}[2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}]\text{I}$	2096 2018 1993	—

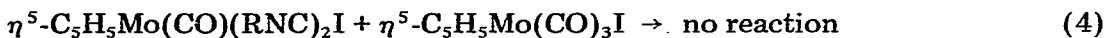
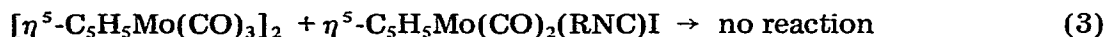
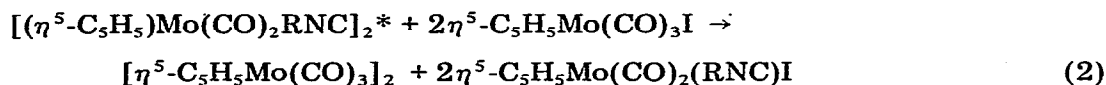
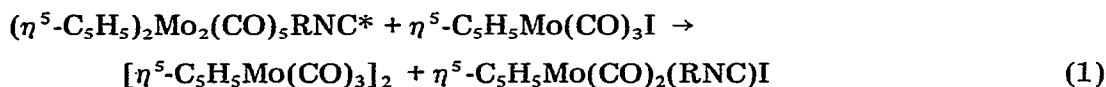
^a In C_6D_6 solution.

The catalytic reaction can readily be extended to the preparation of a wide variety of other analogous complexes such as $\eta^5\text{-C}_5\text{H}_5\text{Mo}[2,6\text{-(CH}_3)_2\text{C}_6\text{H}_3\text{NC}]\text{I}$, $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{CO})_2(\text{PPh}_3)\text{I}$ [7], and $\eta^5\text{-C}_5\text{H}_5\text{W}(\text{CO})_3\text{-}_n(\text{RNC})_n\text{I}$ ($n = 1, 2$). However, no reaction occurred between $\eta^5\text{-C}_5\text{H}_5\text{M}(\text{CO})_3\text{CH}_3$ ($\text{M} = \text{Mo, W}$) and RNC under our reaction conditions.

The rates of the CO substitution reactions are increased by light but are not affected by the addition of radical initiators such as benzoyl peroxide (~5% by mass.). However, the radical scavengers hydroquinone and galvinoxyl inhibit the reaction. The experimental data are consistent with a free radical chain mechanism similar to that proposed by Hoffman and Brown [8], viz.:



This mechanism is further supported by the following observations:



We have also found that the salt $\eta^5\text{-C}_5\text{H}_5\text{Mo}(\text{RNC})_4^+\text{PF}_6^-$ [4] (prepared from II and RNC , followed by addition of NaPF_6) does not catalyse the reaction.

Our studies on the use of transition metals as catalysts in synthetic organo-

*These new complexes have been characterized by IR, NMR and MS and their preparation and characterization will be reported in detail later. See also ref. 3.

metallic chemistry thus reveal that (a) products inaccessible under normal thermal conditions can be obtained by catalytic routes and (b) the use of the catalysts introduces novel reaction pathways.

Acknowledgement

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References

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