Journal of Organometallic Chemistry, 102 (1975) C4—C6
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

MECHANISM OF NUCLEOPHILIC ADDITION TO TRICARBONYL (TROPYLIUM) CATIONS OF METALS IN GROUP VI

K.M. AL-KATHUMI and L.A.P. KANE-MAGUIRE*

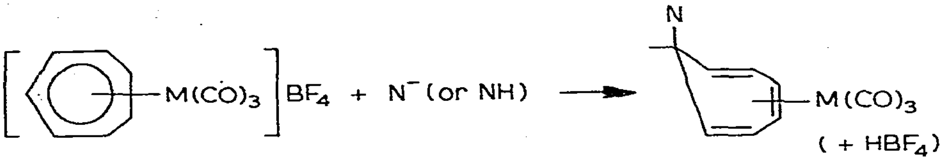
Department of Chemistry, University College, Cardiff CF1 1XL, Wales (Great Britain)

(Received August 19th, 1975)

Summary

A kinetic study of the addition of acetylacetone and methoxide ion to the cations $[(C_7H_7)M(CO)_3]^+$ (M = Cr, Mo, W) reveals only a small dependence of the rate on the nature of the metal, and supports a mechanism involving direct nucleophilic attack at the tropylium rings.

Despite considerable synthetic interest in nucleophilic additions at coordinated π-hydrocarbon ligands, there have been few kinetic investigations of such processes. We report here kinetic data for the addition of methoxide (N^-) and acetylacetone (NH) to the cations $[(C_7H_7)M(CO)_3]^+$ (I: M = Cr, Mo, W; eq.1), which demonstrate the diagnostic value of such studies.



(1)

Eq. 1 is typical of a wide range of nucleophilic additions reported by Pauson and co-workers [1] for tricarbonyl (tropylium) metal cations. The reaction with methoxide ion was studied in water buffered at pH 9.2 to limit hydrolysis of the anion. Although the neutral triene product subsequently precipitated from this solvent mixture, it was possible to follow the rapid methoxide addition using stopped-flow spectrophotometric techniques. On the other hand, the slow addition of acetylacetone (dichloroethane solvent) was monitored by following the disappearance of the strong IR carbonyl band of the cations I at

---

* To whom correspondence should be addressed.

TABLE 1

KINETIC DATA FOR ADDITION OF MeO$^-$ AND ACETYLACETONE ON $[(C_7H_7)M(CO)_3]BF_4$ COMPLEXES

M	Nucleophile	k_{obs} (s^{-1})
Cr	MeO$^-$(0.125 *M*)[a]	13.0
Mo	MeO$^-$(0.125 *M*)[a]	12.2
W	MeO$^-$(0.125 *M*)[a]	17.4
Cr	acacH (2.34 *M*)[b]	5.03×10^{-4}
Mo	acacH (2.34 *M*)[b]	9.52×10^{-4}
W	acacH (2.34 *M*)[b]	11.7×10^{-4}

[a] Water solvent. [b] 1,2-Dichloroethane solvent.

2075 cm^{-1}. Both processes were studied under pseudo-first-order conditions, employing a large excess of nucleophile.

The data in Table 1 show that the rate of addition of both nucleophiles is almost independent of the nature of the central metal, decreasing slightly in the order W > Mo ⩾ Cr. This behaviour contrasts sharply with that observed for related reactions involving nucleophilic attack at Group VI metals, for example reaction 2 which exhibits the relative rate order Mo > W ≫ Cr

$$[(C_7H_7)M(CO)_3]BF_4 + 3\ CH_3CN \rightarrow [(CH_3CN)_3M(CO)_3] + [(C_7H_7)]BF_4 \qquad (2)$$

(85:28:1) [2]. The present results therefore strongly support previous stereochemical evidence [3,4] indicating direct addition of nucleophiles onto the tropylium rings of species I, being inconsistent with a mechanism involving initial rate-determining attack of MeO$^-$ or acetylacetone on the metal.

However, the kinetic data do not exclude a mechanism for reaction 1 involving initial binding of MeO$^-$ or acetylacetone to a carbonyl group. In fact, the relative rates are similar to those found by Werner et al. [5] for the reaction of azide ion on $[M(CO)_6]$ compounds (W > Mo > Cr 7.8:3:1) where the rate-determining step was believed to be attacked by azide ion on a carbonyl group. However, in view of the stereochemical evidence [3,4] indicating general *exo*-addition of nucleophiles in eq. 1, the direct attack mechanism remains favoured.

Finally, our observations conflict with the recent suggestion by Hackett and Jaouen [6] that the tropylium ring in the chromium cation I is more electrophilic than that in its molybdenum analogue. At least towards MeO$^-$ ion and acetylacetone, the chromium and molybdenum species I have very similar electrophilicities (Table 1). The interesting fact that triphenylphosphine replaces a carbonyl ligand from $[(C_7H_7)Mo(CO)_3]^+$ but attacks the tropylium ligand in the analogous chromium cation [6,7] may simply reflect the well-established greater susceptibility of molybdenum complexes towards nucleophilic attack at the metal. In agreement with this view, King and co-workers [8] have observed that the molybdenum and tungsten cations I react with iodide ion to give $[(C_7H_7)M(CO)_2I]$, whereas no reaction occurs with the chromium salt. An explanation for these differences in behaviour may lie in the greater steric freedom present in the molybdenum and tungsten species, and their greater facility for forming seven-coordinate intermediates.

We thank the S.R.C. for the award of a grant for a stopped-flow spectrophotometer.

References

1 J.D. Munro and P.L. Pauson, J. Chem. Soc., (1961) 3475, 3479.
2 K.M. Al-Kathumi and L.A.P. Kane-Maguire, J.Chem. Soc. Dalton, (1973) 1683.
3 P.L. Pauson, G.H. Smith and J.H. Valentine, J. Chem. Soc. (C), (1967) 1061.
4 P.E. Blaikie and O.S. Mills, J. Chem. Soc. (A), (1968) 2704.
5 H. Werner, W. Beck and H. Englmann, Inorg. Chim. Acta, 3 (1969) 331.
6 P. Hackett and G. Jaouen, Inorg. Chim. Acta, 12 (1975) L19.
7 G. Deganello, T. Boschi, L. Toniolo and G. Albertin, Inorg. Chim. Acta, 10 (1974) L3.
R.B. King and A. Fronzaglia, Inorg. Chem., 5 (1966) 1837.