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Preliminary communication

SPECTROSCOPIC EVIDENCE FOR INTERMEDIATES FORMED BY REACTION OF ALKOXIDES WITH $[(\eta^7\text{-}C_7H_7)M(CO)_3]BF_4$ (M = Mo, W)

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Summary

Spectroscopic evidence is presented for low temperature intermediates, involving initial metal attack and carbonyl attack, in the nucleophilic addition of methoxide ions to $[(\eta^7\text{-}C_7H_7)M(CO)_3]BF_4$ (M = Mo, W).

Nucleophilic addition to the cations $[(\eta^7\text{-}C_7H_7)M(CO)_3]BF_4$, (M = Cr, Mo, W) generally forms the 7-*exo*-ring adduct as the stable product [1]. Reaction with alkoxides, in the corresponding alcohol as solvent, invariably produces the 7-*exo* derivative although for M = Mo the methoxy compound has been reported as unstable [2]. The factors influencing the regioselectivity of nucleophilic addition to the above type of cation are still not clear but in a number of related cases, where the final product is the thermodynamically stable ring adduct, evidence has been presented for the existence of intermediates involving initial attack at other sites, for example, the metal or carbonyl group [3—5]. In the preceding paper, a new theoretical approach to regioselectivity is outlined [6]. In this note, we report spectroscopic evidence for metal and carbonyl attack intermediates during the reaction of MeO^- with $[(\eta^7\text{-}C_7H_7)M(CO)_3]BF_4$ (M = Mo, W, complexes I and V) and characterisation of the molybdenum and tungsten 7-*exo*-methoxy complexes, respectively (complexes III and VI).

To the title cation I (0.8 g, 0.002 *M*) in methanol (10 ml) was added sodium methoxide (0.1 g Na in 10 ml methanol). After stirring (10 min) and solvent removal, recrystallization from petroleum spirit (40—60°C) gave orange crystals of compound III, M.p. 86—87°C. Analysis: Found: C, 43.85; H, 3.36. $C_{11}H_{10}MoO_4$ calcd.: C, 43.70; H, 3.31%; Found: *m/e* = 304) The IR spectrum (pentane) showed $\nu(CO)$ peaks at 2000, 1941 and 1919 cm^{-1}. The ^1H NMR spectrum ($CDCl_3$) showed multiplets at 5.92 (H(3,4)), 5.18 (H(2,5)), 4.19

(H(1,6,7)) and 3.04 ppm (OCH_3) with $J_{6,7} \sim 7.3$ Hz confirming the *exo* configuration for III [1]. The tungsten analogue was prepared similarly and gave satisfactory analytical and spectroscopic data. Both products were stable when stored at low temperature under N_2.

To cation I (0.7 g, 0.002 *M*) dissolved in CH_2Cl_2 (15 ml) at —15°C, a slurry of sodium methoxide (prepared as a solid from sodium (1.5 g) in MeOH (20 ml) and subsequent solvent removal) in CH_2Cl_2 (20 ml) at —15°C was added. After stirring briefly (< 1 min), a sample was removed for immediate IR analysis in the region 1550—2200 cm^{-1}, using low temperature cells. The initial spectrum showed peaks at 2005 and 1957 cm^{-1} (Fig. 1a) with virtually no absorption from cation I (ν(CO) 2081, 2025, 1976 cm^{-1}). After 10 min, a second reaction sample was removed and in addition to the two peaks above, three new peaks occurred at 1996, 1926 and 1896 cm^{-1} (Fig. 1b) due to the 7-*exo* product $C_7H_7OMeMo(CO)_3$ (verified by comparison with the spectrum of an authentic sample). On allowing the sample to warm up in the IR cell, the bands at 2005 and 1957 cm^{-1} decreased in intensity; those of the 7-*exo* ring product increased and two new peaks at 1986 and 1631 cm^{-1} appeared (Fig. 1c). After 50 min, the peaks at 2005 and 1957 cm^{-1} disappeared (Fig. 1d) and after 3 h only those peaks due to the 7-*exo* ring product remained (Fig. 1e).

The peaks at 2005 and 1957 cm^{-1} are attributed to an intermediate (II) formed by direct attack (or association) of the MeO^- on the metal atom. This metal-attack intermediate (II) then dissociates to give both the 7-*exo* ring product III and the carbomethoxy compound $(\eta^7\text{-}C_7H_7)Mo(CO)_2(CO_2Me)$ (IV) with bands at 1986 and 1631 cm^{-1} (a third CO band is probably hidden under the lower bands of the ring product). The carbomethoxy compound IV is stable for about 24 h at low temperatures but rearranges rapidly to the ring product III at room temperature and could not be isolated pure.

Corresponding to the infrared studies, complementary ^1H NMR studies in CD_2Cl_2 were made. At the very early stages of reaction corresponding to the intermediate II, a sharp singlet at 5.34 ppm (0.88 ppm upfield from cation I) occurs which disappears with time to give peaks at 5.94 (H(3,4)), 5.19 (H(2,5)) 4.21 (H(1,6,7)) and 2.98 ppm (OCH_3) due to the 7-*exo* ring adduct III (verified by comparison with that of the pure product). No ring proton peak of the carboalkoxy product IV was observed although it may be obscured by a solvent peak at 5.32 ppm. A small singlet at 2.91 ppm may be due to the methoxy group of IV. The initial appearance of a sharp singlet at 5.34 ppm, attributable to the metal-attack intermediate II suggests equivalent ring protons and preservation of electron delocalisation in the ring moiety in II. This implies either rapid fluxionality of the ring or possibly a 20-electron system for the intermediate II.

A dissociative rearrangement is suggested by the exclusive formation of the 7-*exo* ring adduct III. An intramolecular rearrangement would be expected to yield a measurable quantity of the 7-*endo* ring adduct, which was not detected throughout the reaction.

A similar reaction was performed using pentane as solvent. The change in solvent polarity had no effect on the initial site of attack (metal attack) although the rate of reaction increased. Two strong peaks at 2015 and 1974 cm^{-1}, corresponding to metal attack, were observed and disappeared within 2 min to

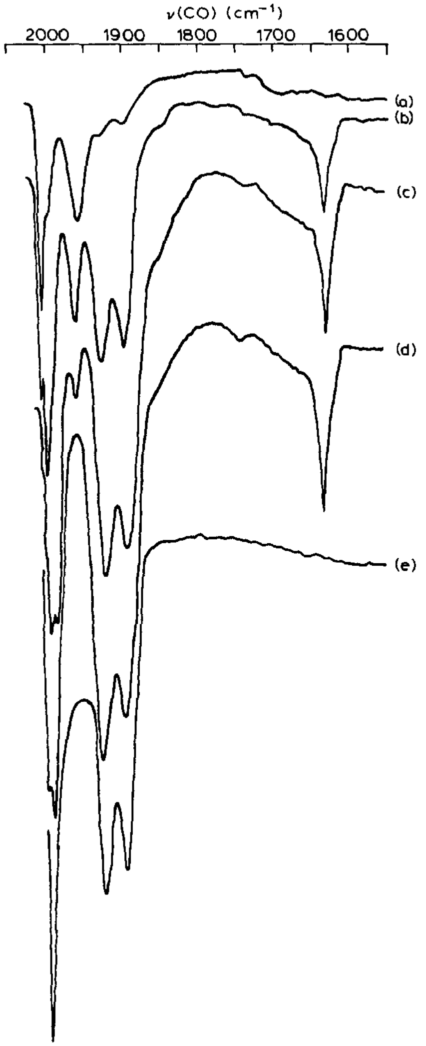

Fig. 1. Low temperature spectra recorded on Perkin—Elmer 283B IR Spectrometer. (a) Initial spectrum after 1 minute, (b) 2nd sample after 10 minutes, (c) 2nd sample after 30 minutes, (d) 2nd sample after 50 minutes, and (e) 3rd sample after 3 h.

leave three peaks at 2000, 1941, and 1919 cm^{-1} corresponding to the 7-*exo* ring adduct.

Similar results were obtained using the $[(\eta^7\text{-}C_7H_7W(CO)_3]^+$ (V) cation in CH_2Cl_2 solvent where initial metal attack was observed. No detectable intermediates were observed using the chromium analogue where only formation of the 7-*exo* ring product was found.

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