Journal of Organometallic Chemistry, 129 (1977) C19—C21
© Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

THE MECHANISM OF NUCLEOPHILIC ATTACK ON $C_6H_7Os(CO)_3^+$ BY OMe^- AND HOMe; A NOVEL REARRANGEMENT OF A CARBOMETHOXY INTERMEDIATE

ERIC G. BRYAN, AUBREY L. BURROWS, BRIAN F.G. JOHNSON, JACK LEWIS*, and G. MARIO SCHIAVON

University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)

(Received January 14th, 1977)

Summary

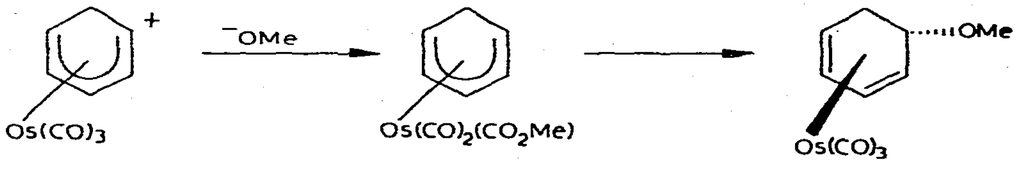
Tricarbonyl(cyclohexadienylium)osmium reacts with methoxide ion to give the carbomethoxy complex $C_6H_7Os(CO)_2(CO_2Me)$ which on heating undergoes stereospecific rearrangement to 5-*exo*-$C_6H_7OMeOs(CO)_3$, but 5-*endo*-$C_6H_7OMeOs(CO)_3$ is the major product when the dienylium complex is treated with methanol.

In contrast to previous views we have recently shown [1] that nucleophilic attack of a variety of alcohols upon tricarbonyl(cyclohexadienylium)iron leads to the formation of the *endo* isomer and not, as previously thought, exclusively the *exo* isomer. The mechanism by which *endo* addition occurs is not clear; one possibility involves initial attack at a coordinated carbonyl group to give a carboalkoxy derivative followed by intramolecular migration to the *endo* face of the dienylium ligand. We have previously shown [2] that the reaction of methoxide with tricarbonyl(cyclohexadienylium)ruthenium occurs via a carbomethoxy intermediate, $C_6H_7Ru(CO)_2(CO_2Me)$, which rearranges to give an unstable ring-substituted product of unknown stereochemistry. The analogous intermediate is observed in the reaction of methoxide ion with tricarbonyl(cyclohexadienylium)iron [3]. We now report the preparation of tricarbonyl(cyclohexadienylium)osmium and its reactions with methoxide ion, or methanol, to give the *exo* and *endo* isomers of tricarbonyl(5-methoxycyclohexa-1,3-diene)osmium, respectively.

On heating triosmium dodecacarbonyl ($Os_3(CO)_{12}$) with cyclohexa-1,3-diene organometallic cluster compounds based on the Os_3 unit are obtained. In contrast, on photolysing a solution of $Os_3(CO)_{12}$ in benzene, in the presence of excess cyclohexa-1,3-diene for 60 hours at 20°C, a 45% yield of the monomeric complex tricarbonyl(cyclohexa-1,3-diene)osmium (I) is obtained. This complex which is a colourless oil has been characterised on the basis of its spectroscopic properties and chemical reactions. Treatment of I with an equimolar quantity of tritylium cation in methylene chloride gives tricarbonyl(cyclohexadienylium)-osmium (II), as a white solid, isolated as the tetrafluoroborate salt. This compound was characterised on the basis of spectroscopic properties and elemental analysis.

The dienylium cation II undergoes nucleophilic addition on treatment with sodium methoxide in methanol at 0°, to give the carbomethoxy complex III, as a white solid. Support for the structure of this complex is obtained from its ^{1}H NMR spectrum, which displays multiplets at τ 3.72 (H(3)), 4.97 (H(2,4)), 6.28 (H(1,5)), 6.85 (H(6)), 7.65 ppm (H(6)), very similar to that of II except that the protons are shielded to a greater extent in the neutral complex and are hence at higher field. A singlet at 6.56 ppm assigned to the methyl protons of the methoxy group together with a band at 1635 cm^{-1} in the IR spectrum of this complex assigned to an ester carbonyl group confirms that the methoxide ion initially attacks at a coordinated carbonyl group of II. The ^{1}H NMR and IR spectra of III are very similar to those of the ruthenium analogue [2].

The carbomethoxy complex III is stable at 0°C, but on heating in organic solvents, or in the solid state, it undergoes stereospecific rearrangement to give the ring-substituted product tricarbonyl(5-*exo*-methoxycyclohexa-1,3-diene)osmium (IV). This compound was identified on the basis of spectroscopic and chemical properties. Thus, the mass spectrum of IV exhibits a strong peak corresponding to the fragment ion $(M - CO - H_2)^+$, while that due to $(M - CO)^+$ was relatively weak; this fragmentation pattern is typical of *exo* isomers [1, 4]. Moreover, the ^{1}H NMR and IR spectra of IV were very similar to those of the corresponding 5-*exo*-methoxy derivative of iron [1], obtained as the stereospecific product of the reaction of tricarbonyl(cyclohexadienylium)iron with methoxide ion. The protonation of IV with HBF_4 in propionic anhydride at 0°C yielded II. The rearrangement of III to give IV was followed by ^{1}H NMR and a linear first-order rate plot was obtained for the reaction. This rearrangement would therefore appear to proceed either via an intramolecular transfer of methoxide from the coordinated group to the *exo* face of the dienylium ligand, or via a dissociative mechanism to give II and methoxide ion, which rapidly adds to the dienylium ring to give the *exo* isomer IV (reaction scheme 1).

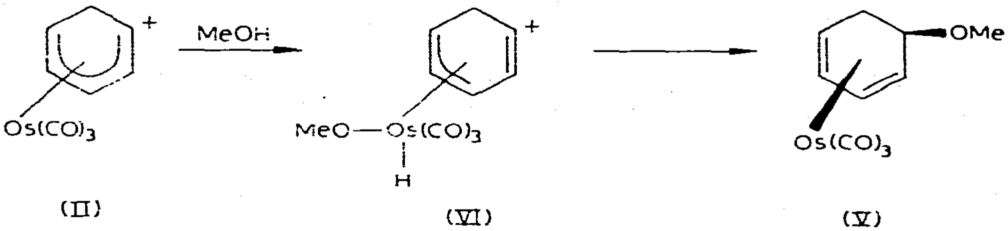


(II) (III) (IV)

SCHEME 1

The *endo* isomer of tricarbonyl(5-methoxycyclohexa-1,3-diene)osmium (IV) has been obtained as the major product of the reaction of the dienylium complex II in refluxing methanol. This compound was identified on the basis of spectroscopic and chemical properties. Thus the mass spectrum of V displays strong peaks corresponding to the fragment ion $(M - CO)^+$ and $(M - CO - MeOH)^+$, while that due to $(M - CO - H_2)^+$ was relatively weak; this fragmentation pattern is typical of *endo* isomers [1]. The ^1H NMR and IR spectra of V are very similar to those of the corresponding 5-*endo*-methoxyiron derivative, which has been previously prepared from the reaction of tricarbonyl(cyclohexadienylium)-iron with refluxing methanol [1]. The protonation of V with HBF_4 in propionic anhydride at 0°C yielded II.

It is clear that the initial attack of methoxide ion on the osmium cation II occurs at a coordinated carbonyl group. In contrast to our previous ideas on the mechanism of *endo* addition it would appear that V is not formed by a simple intramolecular migration of methoxide ion. The formation of the *endo* isomer only occurs in the reaction of methanol with II, and as an alternative reaction sequence to that previously proposed we might consider that the reaction proceeds via the oxidative addition of methanol to the metal according to Scheme 2.



SCHEME 2

The intermediate in this reaction sequence is the allyl cation VI. The generation of this coordinatively unsaturated species by the simple removal of a coordinated olefin fragment is not unreasonable and is regarded as the intermediate in the reaction of tricarbonyl(cycloocta-1,3-diene)iron with phosphine [5]. Finally, we emphasise although the iron system behaves in the same stereochemical way as the osmium system no carbomethoxy intermediate of the type $C_6H_7Fe(CO)_2(CO_2Me)$ has been isolated, but evidence for its intermediacy in the reaction between tricarbonyl(cyclohexadienylium)iron and methoxide ion has been obtained by IR spectroscopy [3].

We wish to thank the S.R.C. for financial support and also Johnson, Matthey and Company Limited for the loan of OsO_4.

References

1 K.E. Hine, B.F.G. Johnson and J. Lewis, Chem. Commun., (1975) 81.
2 R.J.H. Cowles, B.F.G. Johnson and J. Lewis, Chem. Commun., (1969) 392.
3 A.L. Burrows, unpublished results.
4 M.A. Haas and J.M. Wilson, J. Chem. Soc. B, (1968) 104.
5 B.F.G. Johnson, J. Lewis and M.V. Twigg, J. Chem. Soc. (Dalton), (1974) 2546.