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Preliminary communication

NUCLEOPHILIC ATTACK ON TRICARBONYL(CYCLOHEXADIENYL)OSMIUM; FORMATION OF A SIX-MEMBERED σ—η-ALLYL PRODUCT

AUBREY L. BURROWS, BRIAN F.G. JOHNSON, JACK LEWIS and DAVID G. PARKER*
University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (Great Britain)
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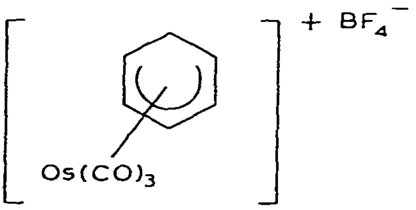
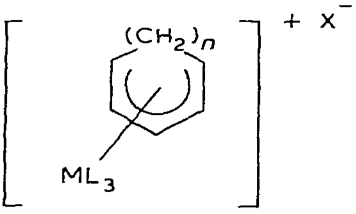
Summary

A study of the interaction of tricarbonylcyclohexadienylosmium (I) with a series of nucleophiles has revealed a considerable variation in the site of attack. Thus hydride and cyanide ions attack I to give both 1,3-diene- and allyl-bonded products, while amines, alcohols, thiols, phosphines and carbon nucleophiles other than cyanide give exclusively 1,3-diene derivatives.

Nucleophilic addition to a coordinated dienyl complex of type II is known to occur at the 1[1], 2[1] or 3[2] positions, depending on the ring size, the metal and auxiliary ligands present in the complex. Addition to the 2 position has been reported [1] to occur for the 7- and 8-membered dienyl complexes but not the 6-membered analogues. We now find that nucleophilic addition can occur at the 2-position of the 6-membered tricarbonylcyclohexadienylosmium (I), to give stable σ—η-allyl products.



(I)



(II)

n = 1, 2, 3;

M = Fe, Ru, Os;

L = CO, PH_3, etc.;

$X^- = BF_4^-, PF_6^-$

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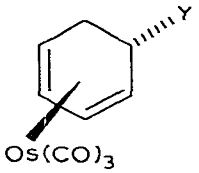
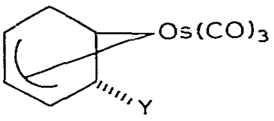
*Present address: ICI Petrochemicals, PO Box 90, Wilton, Middlesborough, Cleveland TS6 8JE (Great Britain)

Reduction of I with sodium borohydride in water yielded two products in approximately equal amounts. These could not be separated by chromatography, but were identified as the 1,3-diene complex III (Y = H) and the σ—η-allyl derivative IV (Y = H).



(III)

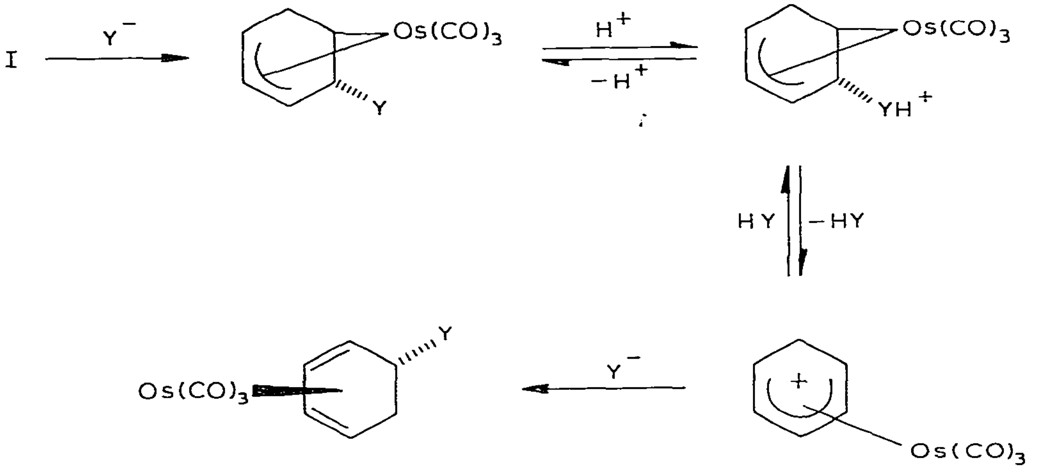


(IV)

The ^1H NMR spectrum of this mixture displayed characteristic multiplets at τ 4.50, 6.72 and 8.44, readily assignable to the inner, outer and methylene protons of the known tricarbonylcyclohexa-1,3-dieneosmium (III, Y = H) [3]. The spectrum also contained a sharp doublet at τ 5.06 assigned to the outer protons of the allyl of IV (Y = H) together with a multiplet at τ 5.38 due to the centre allyl proton. The centre allyl proton usually appears at lower field than the outer allyl protons for 7- and 8-membered σ—η-allyl derivatives [1] but the reverse pattern observed here probably results from the strained nature of the product. The methylene *exo* and *endo* protons of IV (Y = H) occur at τ 7.00 and 8.19, respectively, and the spectrum is completed by a one-proton multiplet at τ 9.06 assigned to the σ-bonded carbon proton. The mass spectrum of this mixture gave a single parent peak at 356, together with peaks corresponding to loss of one, two and three carbonyl groups. The IR spectrum of the mixture also supported the presence of two compounds: ν(CO) 2065, 1986, 2060, 1983, 1977 cm^{-1} (C_6H_{12}).

Reaction of the mixture of III (Y = H) and IV (Y = H) with trityl cation regenerated only the dienyl cation I ($\sim$ 92%). Refluxing the mixture in hexane for 5 h resulted in the isomerization of the σ—η-allyl product to the 1,3-diene complex, presumably by a hydrogen atom migration via the *endo* face of the coordinated ligand. This type of isomerization has previously been reported by Aumann (1c) for the 7-membered σ—η-allyl derivative, however, more vigorous reaction conditions were needed (120°C, 15 h). The more facile rearrangement in the case of the 6-membered complex in the present work probably reflects the lower stability of the σ—η-allyl conformation for the 6- over the 7-membered ring.

Reaction of the dienyl complex I with cyanide ion also results in the formation of a σ—η-allyl product IV (Y = CN), together with the corresponding 1,3-diene product III (Y = CN) in the ratio 3/1. However, all other nucleophiles, such as alcohols, thiols, amines, phosphines and carbon nucleophiles other than cyanide ion, yielded only the 1,3-diene product III. The formation of σ—η-allyl products with only hydride and cyanide ions has been observed in other systems [1, 4], and may be a consequence of the "soft" nature of these two nucleophiles [5]. However, since other soft nucleophiles, e.g. thiols, fail to yield σ—η-allyls, a more satisfactory explanation would appear to be that nucleophiles other than H^- or CN^- add reversibly at the inner 2- and 4-positions of the dienyl system to give σ—η-allyl bonded derivatives. These complexes could then rearrange via a dissociative mechanism to regenerate the dienylium cation. Subsequent attack by the nucleophile at the terminal positions of the dienyl system would yield the observed 1,3-diene bonded derivatives as the thermodynamic product:



(V)

The protonated species V would be reasonable for Y = OH, OR, SH, PR_3, $-\overset{O}{\overset{\|}{C}}R$, etc. but not for Y = H or CN.

The results described herein demonstrate that the 1-σ-3—5η-allyl bonding mode is indeed stable for the 6-membered ring. Furthermore, it is clear that the osmium tricarbonyl moiety must exert a dominant influence on the pathway of the reaction. This is consistent with previous reports that dienylosmium tricarbonyl complexes show a greater tendency to form σ—η-allyl derivatives than do the corresponding iron and ruthenium analogues [1a]. The way in which osmium directs attack to the 2-position of the dienyl is not clear, but the more diffuse and flexible nature of the metal orbitals on osmium should stabilise the less planar σ,η-allyl structure over the relatively planar 1,3-diene conformation.

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References

1 (a) A.J. Deeming, S.S. Ullah, A.J.P. Domingos, B.F.G. Johnson, and J. Lewis, J. Chem. Soc. Dalton, (1974) 2093; (b) R. Edwards, J.A.S. Howell, B.F.G. Johnson and J. Lewis, ibid., (1974) 2105.
2 B.F.G. Johnson, J. Lewis, T.W. Matheson, L.E. Ryder and M.V. Twigg, J. Chem. Soc. Chem. Commun., (1974) 269.
3 E.G. Bryan, A.C. Burrows, B.F.G. Johnson, J. Lewis and M.G. Schiavon, J. Organometal. Chem., 129 (1977) C19.
4 J. Evans, B.F.G. Johnson, and J. Lewis, J. Chem. Soc. Dalton, (1972) 2668.
5 R.G. Pearson, Chem. Brit., (1967) 103.