Journal of Organometallic Chemistry, 90 (1975) C31—C33

Preliminary communication

THE REACTION OF *cis*-BICYCLO[6.2.0]DECA-2,4,6-TRIENE WITH DODECACARBONYLTRIRUTHENIUM

G. DEGANELLO

Centro Chimica Tecnologia Composti Metallorganici Elementi Transizione - C.N.R. - Facoltà Chimica Industriale, Università di Venezia, Calle Larga S. Marta 2137, Venezia (Italy)

P.L. SANDRINI and R.A. MICHELIN

Cattedra di Chimica, Facoltà di Ingegneria, Via F. Marzolo 9, Università di Padova, Padova (Italy)

L. TONIOLO

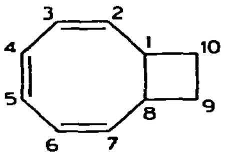
Istituto di Chimica Generale, Università di Padova, Padova (Italy)

(Received February 17th, 1975)

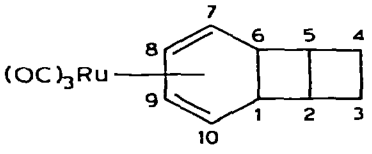
Summary

The major products of the reaction of Ru$_3$(CO)$_{12}$ with *cis*-bicyclo[6.2.0]-deca-2,4,6-triene are (7-10-η-tricyclo[4.4.0.0^{2,5}]deca-7,9-diene)tricarbonylruthenium and (the fluxional) *cis*-bicyclo(2,6,7-η, 3-5-η-bicyclo[6.2.0]deca-2,4,6-triene) hexacarbonyldiruthenium (Ru—Ru).

Since the first report of the reaction of a metal carbonyl with a triene [1], there have been several investigations of such reactions particularly in the field of iron carbonyl complexes of cyclic polyolefins and their metal promoted skeletal rearrangements [2]. The corresponding reactions of ruthenium carbonyls with cyclooctatetraene [3], cyclooctatriene [4], and cycloheptatriene [5] have been described recently. We report below some preliminary results on the reaction of Ru$_3$(CO)$_{12}$ with *cis*-bicyclo[6.2.0]deca-2,4,6-triene (I). Two major products*, II and III, have been isolated from the reaction in boiling toluene.



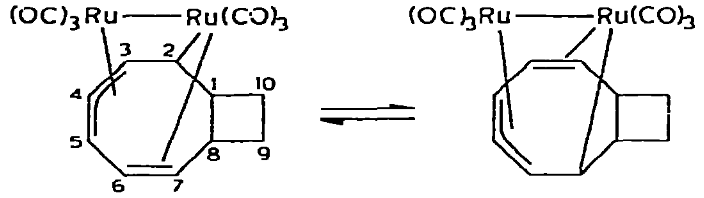
(I)



(II)

---

*II and III gave correct elemental analysis. Four other minor products have been separated and will be described in the full paper.



(III)

II, white sublimable needles in 47% yield, (m.p. 86-88°C, IR ν(CO) 2061, 1997, 1990 cm^{-1} in hexane solution) shows in the ^{1}H NMR spectrum a pattern similar to that of the corresponding 7-10-η-tricyclo[4.4.0.0^{2,5}]deca-7,9-diene tricarbonyliron [6, 7] (τ 4.48 (H^{8,9}), 6.48 (H^{7,10}), 7.42-7.80 (H^{1,6}, H^{2,5}), 7.80-8.35 (H$^{3,3'}$, H$^{4,4'}$) in CDCl$_3$ solution). The similarity of ^{1}H NMR spectra of II and the iron analog strongly indicates that for II also there is an *exo*-conformation of the three rings, the cyclohexadiene moiety being *cis* fused to a cyclobutane ring, which in turn is *cis*-fused to another 4-membered ring [8].

III, a yellow crystalline compound (m.p. 117-119°C, yield 20%) shows IR bands [ν(CO)] at 2072, 2036, 2008, 1997, 1985(sh), 1980 cm^{-1} in hexane solution. At room temperature its ^{1}H NMR spectrum in CDCl$_3$ is consistent with the presence of a molecular plane of symmetry [τ 5.48 m (H^{4,5}), 5.82m (H^{3,6}), 7.44s (H^{1,8}), 7.52d (H^{2,7}, $J_{2,3} = J_{6,7} = 8.6$ Hz), 8.07m (H$^{9,9'}$, H$^{10,10'}$)]. The limiting spectrum corresponding to configuration III is reached at −115°C (CS$_2$ solution), suggesting a higher activation energy than that of the iron analog for the interconversion of the two enantiomers [9].

Indeed on the basis of the data available the intermediacy of an η^4-Ru(CO)$_3$ complex of I as precursor to II cannot be ruled out. In the corresponding iron chemistry the stability of η^4 1,3- and 1,5-bonded triene Fe(CO)$_3$ complexes is in favour of the suggestion of trapping of the tricyclic diene moiety [6, 7, 10] and this may be also the case of our reaction. Further studies are in progress to discriminate between these two possibilities.

Under the same experimental conditions (boiling toluene) the corresponding dinuclear iron complex of III undergoes rearrangement to the iron analog of II [6]. Since a similar ratio in the yield of II and III is obtained also when the reaction is carried out in boiling n-hexane (the reaction is however much slower, since ≃ 40% of Ru$_3$(CO)$_{12}$ is recovered after three days) it appears that II is not appreciably formed by thermal rearrangement of III. We are now studying the thermolysis of III to see if the other minor products of the reaction originate from its rearrangement.

References

1 E.W. Abel, M.A. Bennet and G. Wilkinson, Proc. Chem. Soc., (1958) 152.
2 For a recent survey see: G. Deganello, P. Uguagliati, L. Calligaro, P.L. Sandrini and F. Zingales, Inorg. Chim. Acta, 13 (1975) in press.
3 F.A. Cotton, A. Davison, T.J. Marks and A. Musco, J. Amer. Chem. Soc., 91 (1969) 6598; see also J.A.K. Howard, S.A.R. Knox, V. Riera, F.G.A. Stone and P. Woodward, J. Chem. Soc. Chem. Commun., (1974) 452; R. Bau, B. Chaw-Kuo Chou, S.A.R. Knox, V. Riera and F.G.A. Stone, J. Organometal. Chem., 82 (1974) C43.

4 A.C. Szary, S.A.R. Knox and F.G.A. Stone, J. Chem. Soc., Dalton Trans., (1974) 662.
5 R. Bau, J.C. Burt, S.A.R. Knox, R.M. Laine, R.P. Phillips and F.G.A. Stone, J. Chem. Soc. Chem. Commun., (1973) 726.
6 F.A. Cotton and G. Deganello, J. Organometal. Chem., 38 (1972) 147; J. Amer. Chem. Soc., 94 (1972) 2142.
7 G. Sholes, C.R. Graham and M. Brookhart, J. Amer. Chem. Soc., 96 (1974) 5665.
8 F.A. Cotton and J.M. Troup, J. Organometal. Chem., 77 (1974) 369.
9 F.A. Cotton, B.A. Frenz, G. Deganello and A. Shaver, J. Organometal. Chem., 50 (1973) 227.
10 G. Deganello, H. Maltz and J. Kozarich, J. Organometal. Chem., 60 (1973) 323; E.J. Reardon Jr. and M. Brookhart, J. Amer. Chem. Soc., 95 (1973) 4311.