Journal of Organometallic Chemistry, 54 (1973) C17–C18
© Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

A π-allyl to σ-allyl rearrangement: The isolation of (di-π-cyclopentadienyl)-(σ-allyl)(carbon disulphide)niobium and its reaction with alkyl halides

G.W.A. FOWLES, L.S. PU and D.A. RICE

Department of Chemistry, University of Reading, Whiteknights, Reading RG6 2AD (Great Britain)

(Received April 3rd, 1973)

SUMMARY

A π-allyl to σ-allyl rearrangement occurs when $(\pi\text{-}C_5H_5)_2(\pi\text{-allyl})Nb$ reacts with CS_2 to give $(\pi\text{-}C_5H_5)_2(\sigma\text{-allyl})Nb(CS_2)$ (I); I reacts with RI to give $(\pi\text{-}C_5H_5)_2(\sigma\text{-allyl})Nb(CSSR)I$.

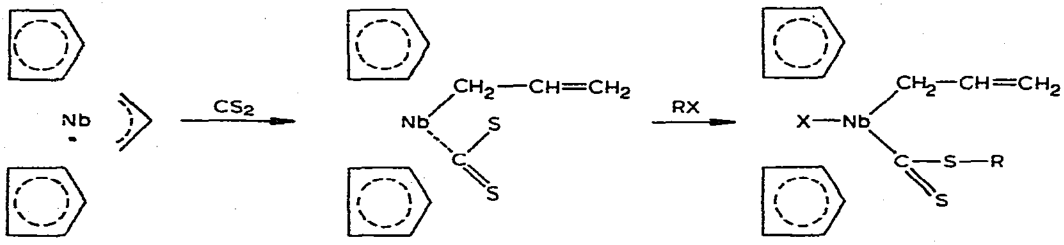
$\pi \rightarrow \sigma$-allyl rearrangements have been postulated to explain the NMR of various transition metal species in solution. Such rearrangements are said to take place when π-allyl complexes are used in catalytic processes involving the coordination of alkenes.

When $(\pi\text{-}C_5H_5)_2(\pi\text{-allyl})Nb^1$ is dissolved in CS_2 it gives a red-violet solution from which red crystals of $(\pi\text{-}C_5H_5)_2(\sigma\text{-allyl})Nb(CS_2)$ (I) may be isolated in 70% yield. The σ-bonded nature of the alkyl group has been established by infrared and NMR spectra (in CS_2); the infrared spectrum of I shows a characteristic[1] ν(C=C) at 1605 cm^{-1} and the NMR spectrum contains typical resonances at τ 7.27 ($-CH_2-$ doublet $J(CH_2-CH)$ 8 Hz), 5.5 ($=CH_2$ complex) and 4.1 ($-CH=$complex). The NMR spectrum further shows the expected single cyclopentadienyl resonance at τ 4.83, while the infrared spectrum[2,3] confirms the presence of a bonded carbon disulphide molecule with a ν(C=S) band at 1135 cm^{-1}.

The presence of a σ-allyl group in I has also been shown by a single crystal X-ray study[4].

In toluene solution, I reacts with an excess of alkyl iodide at room temperature to give ca. 50% yield of yellow crystals (II) of formula $(\pi\text{-}C_5H_5)_2(\sigma\text{-allyl})Nb(CSSR)I$ ($R = CH_3$, C_2H_5, n-Pr, n-Bu). The infrared spectra of II shows ν(C=C)(σ-allyl) ca. 1610 cm^{-1} as well as C–S–C modes ca. ν(C=S) 1120s, $\nu(C{-}S)_{anti}$ 770m, $\nu(C{-}S)_{sym}$ 670w, associated with a dithioalkyl ester group. The ^1H NMR spectrum of the species formulated as II shows characteristic σ-allyl resonances (τ 7.03 ($-CH_2-$ doublet $J(CH_2-CH)$ 8Hz), 5.1. ($=CH_2$ complex), 3.7 ($-CH=$ complex), the resonances commensurate with the nature of R and a singlet assignable to π-C_5H_5 (τ 4.01). Chemical evidence for the nature of II is provided by the reaction of II ($R = CH_3$) with dilute hydrochloric acid, which yields propene as the only gaseous product. Satisfactory chemical analyses were obtained for the species reported.

Reaction of I with alkyl chlorides does not yield isolable products but by reaction of I with ethyl bromide at a higher temperature and for a longer period than for the alkyl iodides, [60°C for 2 h] gives a 30% yield of $(\pi\text{-}C_5H_5)_2(\sigma\text{-allyl})Nb(CSSEt)Br$. Both I and species of type II are remarkably stable in the solid state for compounds containing early-transition metal—carbon σ bonds, and may be heated to 100°C without decomposition. They may also be exposed to the atmosphere for several weeks without detectable change. In solution however, they are considerably less stable.



(I) (II)

REFERENCES

1 F.W. Siegent and H.J. de Liefde Meijer, *J. Organometal. Chem.*, 23 (1970) 177.
2 M.C. Baird and G. Wilkinson, *J. Chem. Soc. (A)*, (1967) 865.
3 D. Commereuc, I. Doucek and G. Wilkinson, *J. Chem. Soc. (A)*, (1970) 1771.
4 M.G.B. Drew, to be published.