

Carbon–Carbon Triple-bond Fission in the Homogeneous Catalysis of Acetylene Metathesis

G. Jeffery Leigh,* Mohammed T. Rahman, and David R. M. Walton

School of Molecular Sciences, University of Sussex, Brighton BN1 9QJ, U.K.

Experiments with asymmetric acetylenes labelled with ^{13}C at an acetylene carbon confirm that two different homogeneous catalysts for acetylene metathesis bring about carbon–carbon triple-bond fission.

Schrock and co-workers recently reported that carbyne complexes such as $[\text{W}(\text{NPr}^1)_3(\text{CBu}^1)]$ (1) are catalysts for acetylene metathesis reactions.¹ This observation provides valuable support for the idea that the mechanism of acetylene metathesis is analogous to that generally accepted for olefin metathesis (Scheme 1).² We have carried out labelling experiments in an attempt to confirm this inference.

The acetylene (2) (0.95 mmol), labelled as indicated with an enrichment of 40%,[†] was exposed to (1) (0.03 mmol) in dry, degassed toluene (5 cm³) for 1 h at 25 °C. Equilibrium between the three possible acetylenes within this system was established well within this period and at least 97% of the total acetylenes were still present at the end of this time. The acetylenic products (2)–(4) were separated from each other

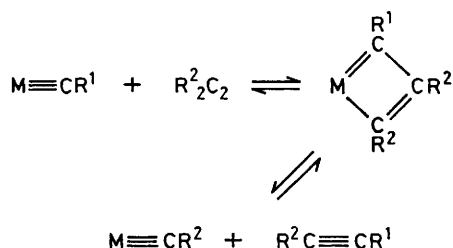
and the reaction mixture by preparative g.l.c.‡ and the ^{13}C contents were determined by quantitative n.m.r. spectroscopy. The acetylene (4) did not contain ^{13}C above natural abundance; all the expected ^{13}C was found in both acetylenic carbon positions of (3), and in the expected position of (2), i.e. adjacent to the phenyl group.



This result demonstrates that acetylene metathesis in this system proceeds entirely by carbon–carbon triple-bond fission, consistent with the proposed mechanism.

The homogeneous catalyst system $[\text{Mo}(\text{CO})_6]\text{-PhOH}$ also catalyses acetylene metathesis in octane solution.³ A mixture of (2), $[\text{Mo}(\text{CO})_6]$, and PhOH in the molar ratios 10:1:1 reached statistical metathesis equilibrium within 2 h, although by this time only 65% of the total acetylenes could be recovered. As with the Schrock catalyst, the enrichment of acetylenic carbon atoms was in quantitative agreement with a process involving only carbon–carbon triple-bond cleavage. These results confirm experiments by Mortreux *et al.*⁴ on the metathesis of ^{13}C -labelled $\text{PhC}\equiv\text{CPh}$ by $\text{Mo}(\text{CO})_6$ and excess of *p*-bromophenol.

This observation implies that the $[\text{Mo}(\text{CO})_6]\text{-PhOH}$ catalyst also operates *via* a carbyne complex mechanism. It is conceivable that such a carbyne complex could be derived from the phenol phenyl group and a carbonyl carbon atom.



Scheme 1

[†] This was prepared by coupling $\text{Ph}^{13}\text{C}\equiv\text{CH}$, 40% enriched (R. F. C. Brown, T. W. Eastwood, K. J. Harrington, and G. L. McMullen, *Aust. J. Chem.*, 1974, 27, 2393), with *p*- $\text{MeC}_6\text{H}_4\text{I}$ in the presence of $[\text{PdCl}_2(\text{PPh}_3)_2]\text{-CuI}$ in Et_3NH (K. Sonogashira, Y. Tohda, and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467).

[‡] Conditions: Pye 105 chromatograph, column 20% OV-101 on Chromosorb P, 7 feet long, 230 °C, carrier gas N_2 at a flow rate of 150 cm³ min⁻¹, injection temperature 250 °C.

However, a series of experiments with various reactant and catalyst ratios showed no evidence of departure from the statistical 1:2:1 equilibrium acetylene ratio[§] which would have arisen from intervention by or introduction of additional PhC groups derived from the catalyst. We conclude either that a catalytic carbyne-species, if involved, is generated in very low amount {*ca.* 1% of the [Mo(CO)₆] or PhOH being involved} or that the constituents of the carbyne function are derived from [Mo(CO)₆] and acetylene alone. This point is now under investigation.

[§] The minimum amount of a given acetylene detectable was *ca.* 0.02% of the total acetylenes present. Amounts of different acetylenes present could be compared with a reliability of $\pm 3\%$.

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