Journal of Organometallic Chemistry, 99 (1975) C47—C48

Preliminary communication

DICHLOROTETRACARBONYLTUNGSTEN AS A CATALYST FOR OLEFIN METATHESIS

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(Received June 30th, 1975)

Summary

The photolysis of hexacarbonyltungsten (I) in carbon tetrachloride yields a catalytic mixture for olefin metathesis. One of the principal products of this transformation is dichlorotetracarbonyltungsten (II). Chemical preparation of II from I and chlorine was carried out. Authentic II was shown to give catalysis of 2-pentene metathesis by either heating in chlorobenzene or chloroform or irradiation in chlorobenzene or carbon tetrachloride. The Dubois report of phosgene formation in the original irradiated mixture of I in carbon tetrachloride was shown to be an artifact.

Investigations of olefin metathesis which aim toward understanding its mechanism or exploiting its synthetic capabilities have been hampered by the experimental inconvenience of manipulating a catalyst of compounds of molybdenum, tungsten or rhenium and a cocatalyst of compounds of aluminum, lithium, tin or magnesium [1]. Recently, two laboratories reported independently a metathesis catalyst which was generated photochemically from hexacarbonyltungsten (I) and carbon tetrachloride [2, 3]. This procedure's simplicity would seem to mandate an intensive examination of this system, which is one of the very few metathesis catalysts without cocatalyst. We have found that dichlorotetracarbonyltungsten (II) is formed in this photochemical process and that it is a catalyst upon thermal or photolytic activation.

The irradiation of $W(CO)_6$ in carbon tetrachloride without olefin leads to a mixture whose infrared spectrum has peaks at 2100m, 2015s, 1976vs and 1940m cm^{-1}. Dubois and his colleagues assigned the first two peaks to $W(CO)_5Cl$ and the latter two peaks to unreacted $W(CO)_6$ and its ^{13}C satellite [2]. They ruled out the presence of II because the aforementioned bands did not match precisely the bands reported [4] for II in chloroform. Since $W(CO)_5Cl$ would be unstable in light of the EAN rule, we prepared II according to the procedure of Bowden and Colton [4]. Its carbonyl absorbancies in carbon tetrachioride were

2100m, 2015s, 1976vs and 1940m cm^{-1}. The intensity ratio of the 1976 band to the 2015 band was greater in the irradiated solution of $W(CO)_6$ due to the presence of unreacted I.

When *cis*-2-pentene (3.0 mmol) in 3 ml chlorobenzene was heated with II (0.03 mmol) at 80°C for two hours, the conversion was 85% and the selectivity to 2-butenes and 3-hexenes was 85%. Replacement of chlorobenzene with 3 ml chloroform afforded the same conversion and selectivity under the same conditions.

Replacement of chlorobenzene with carbon tetrachloride, however, did not lead to metathesis. Chlorinated products were obtained and their composition is being examined.

When another chlorobenzene solution of *cis*-2-pentene and II in the same amounts as above was irradiated overnight in a Rayonet reactor (2537 Å), the conversion of the olefin was 35% and the selectivity to metathesis products was 65%. Replacement of chlorobenzene with carbon tetrachloride with the same quantities and conditions gave 40% conversion and 73% selectivity. Heating II at 60°C for three hours in chlorobenzene or overnight irradiation of it in chlorobenzene without olefin did not cause its decomposition as gauged by the lack of change in the IR spectra.

The presence of II in other catalytic systems has been inferred in those tungsten-containing catalysts formed by reductive carbonylation of halides and oxyhalides with ethylaluminum dichloride [5, 6]. Similar spectral inferences can be drawn for the evaporated benzene solutions of the ethylaluminum dichloride and (acetonitrile) pentacarbonyltungsten system [7].

In contrast to the Dubois work we did not observe a phosgene band at 1812 cm^{-1} in the irradiated solution of $W(CO)_6$ in carbon tetrachloride. Since we had deoxygenated the solvent by the freeze—thaw technique, we repeated our work using an unpurified carbon tetrachloride sample and noted formation of the 1812 cm^{-1} band. This peak grew in intensity when oxygen was bubbled through the solution prior to irradiation. This formation of phosgene had been reported by Silverman and Olofson [8], who noted that the source of the carbonyl group in the phosgene is the carbon tetrachloride and not any of the carbonyls of I. Thus phosgene formation is not related to events leading to a metathesis catalyst.

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