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**Preliminary communication**

**THE C=C DOUBLE BOND OF A BIDENTATE CARBENE-ALKENE COMPLEX OF TUNGSTEN AS AN INTERNAL NMR PROBE FOR THE COORDINATION OF LEWIS ACIDS**

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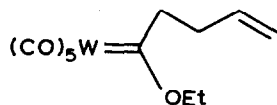
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**Summary**

The rate of polymerization of alkynes induced by tungsten complexes containing a coordinated C=C double bond can be considerably enhanced by Lewis acids such as  $\text{AlR}_3$ . The interaction of the two catalyst components studied by means of NMR spectroscopy, leads to a weakening of the bond between the metal and the double bond.

Carbene complexes of tungsten containing a coordinated C=C double bond can be used for catalysis of oligomerization and polymerization reactions of alkynes [1,2]. The activity of these special Fischer carbene complexes can be accounted for in terms of a ready decoordination of the double bond by the incoming alkynes, and so any process able to labilize the coordinated double bond should greatly enhance the activity. The purpose of this communication is to show that alkylaluminum compounds can enhance the activity in this way and furthermore that the nature of the interaction between  $\text{AlR}_3$  and the carbene complex can be established by means of  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy.



( 1 )

Experiments of a type previously described [3] showed that whereas complex 1 alone or associated with  $\text{AlR}_3$  does not react with alkynes, the rate of ethyne and

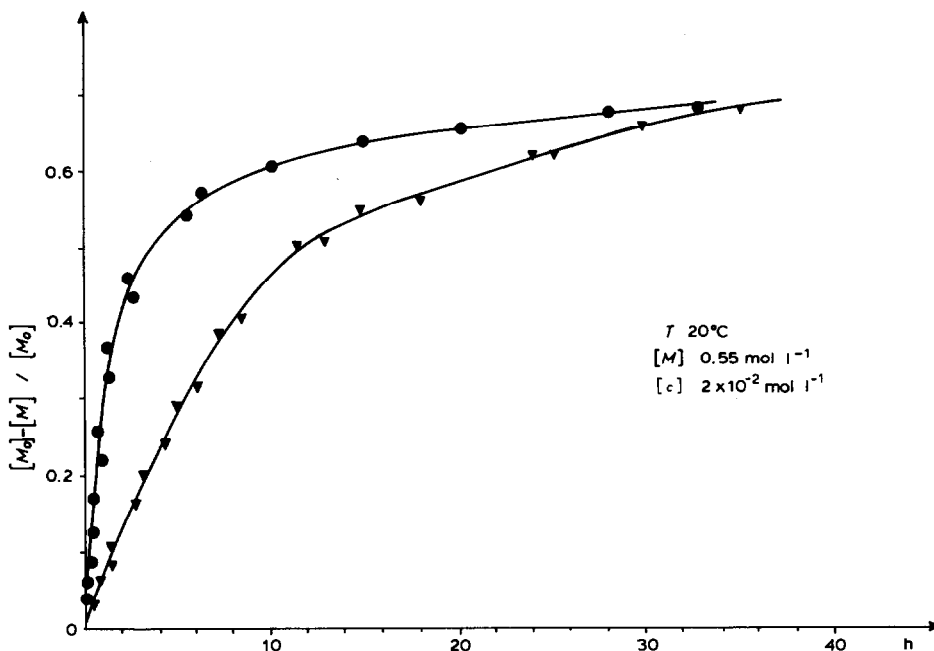
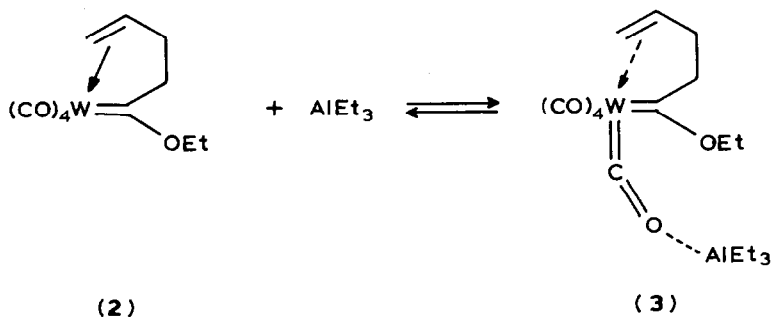


Fig. 1. Plot of the extent of conversion against time for the polymerization of 1-heptyne in hexane, at 20°C.  $\blacktriangle$ , initiation by **2**;  $\bullet$ , initiation by **3**.

1-heptyne polymerizations induced by complex **2**, can be strongly enhanced at room temperature by the presence of  $\text{AlR}_3$ , as shown in Fig. 1.

The interaction of  $\text{AlR}_3$  and complex **2** was monitored spectroscopically. There was no change in the UV spectrum of complex **2** upon addition of  $\text{AlR}_3$ , which means that no major chemical change is involved in the interaction, but there were important chemical shift changes in the  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra (Table 1, Fig. 2) (Al/W 6).



These changes involve almost exclusively the chemical shifts of the atoms of the double bond and of one of the coordinated CO groups. The overall result is a deshielding of the signals which implies that the coordination of the double bond in complex **3** is weaker than in complex **2**. The fact that one CO group is deshielded means that the site of fixation of  $\text{AlR}_3$  in the complex is probably the oxygen atom

TABLE 1

$^1\text{H}$  AND  $^{13}\text{C}$  NMR DATA FOR COMPLEXES 2 and 3 (chemical shifts (ppm) relative to TMS; solvent  $\text{C}_6\text{D}_{12}$ )

	Complex	C(4)H	C(6)H <sub>2</sub>	C(5)H <sub>t</sub>	C(5)H <sub>c</sub>	C(2)H <sub>2</sub>	C(1)	CO <sub>ris</sub>	CO <sub>trans</sub>	
									W=C	C=C
$^1\text{H}$	2	5.23	4.70	3.36	3.27	2.84				
	3	5.60	4.70	3.87	3.67	2.84				
$^{13}\text{C}$	2	86.2	79.7	57.7		52.9	341.2	203-204	211	213
	3	96.5	81.3	66.1		53.4	342.2	201-202	208	223

of the CO group *trans* to the double bond. As a result, the electron density on the metal center is lower, and thus the double bond is less strongly coordinated to the metal. As the changes in the chemical shifts are dependent on the ratios Al/W, it is probable that there is an equilibrium between 2 and the associated form.

Activation of Fischer type carbene complexes by Lewis acids stronger than  $\text{AlR}_3$  (e.g.  $\text{TiCl}_4$ ) has been observed previously in the polymerization of cycloolefins [4], but the exact role and the fate of the carbene fragment were not determined, although opening of a coordination site by expulsion of a CO ligand was suggested. In the case of complex 2, it again seems that the requirement for the insertion

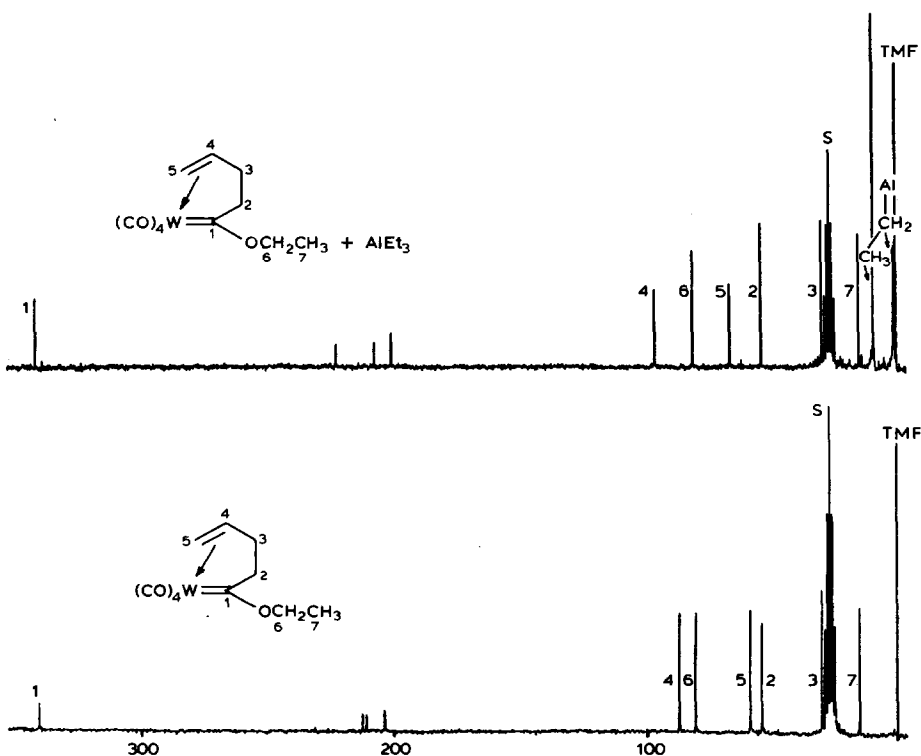


Fig. 2. NMR spectra of 2 and 3 in  $\text{C}_6\text{D}_{12}$  (JEOL FX 90).

reactions is the presence of the coordinated double bond, which, is more or less strongly coordinated to the metal center depending upon the reaction conditions.

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