I.R. Spectroscopic Studies on Polymer-bonded (η^5-C_5H_5)W(CO)$_3$H. A Precursor for a Reusable Catalyst Component for the Olefin Metathesis Reaction

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I.r. spectroscopy on their polystyrene-bonded forms indicates that with complexes of the type (η^5-C_5H_5)W(CO)$_3$R (R = H, Cl) olefin metathesis proceeds with preservation of the structural unit (η-C_5H_5)W(CO)$_3$.

Carbonyl complexes of tungsten are particularly suitable for mechanistic studies of the olefin metathesis reaction since the strong i.r. absorption bands facilitate the monitoring of changes in the co-ordination sphere of the metal. The limited success of this approach in the past is due mainly to the complexity of the catalyst systems, which normally require an organometallic non-transition metal compound as a co-catalyst and in many cases an additional activator such as oxygen.

It is now reported that (η^5-C_5H_5)W(CO)$_3$H, when bonded *via* the cyclopentadienyl ligand to polystyrene–2%-divinylbenzene, gives a heterogenized catalyst component of high stability. This complex shows a low rate of metal bleeding under reaction conditions that require isobutylaluminium dichloride as a co-catalyst. In addition, the stable bond between the metal and the insoluble support permits filtration from the complicated reaction mixture, washing, and spectroscopic examination of the remaining tungsten compound. This technique has been used to demonstrate that studies on a polymer-supported Ziegler-type catalyst can yield indications about the ligand sphere that remains in the catalytically active complex. This information then should promote understanding of the nature of the intermediates involved in the catalytic cycle.

Ⓟ-CH_2–C_5H_4-η^5-W(CO)$_3$H was prepared according to the method of Gubitosa and Brintzinger.[1] The resulting polymer, when activated with Cl_2AlBu^i is a highly active catalyst system for the conversion of internal olefins. At a W: olefin : Al molar ratio of 1 : 1000 : 10, simultaneous double bond migration and metathesis of *trans*-hept-3-ene results in a broad carbon number distribution and after one hour 77.5 wt.% of the product consists of olefins other than heptenes. The high stability of the bond between tungsten and polymer is demonstrated in Figure 1. At a W : olefin : Al ratio of 1 : 300 : 7, the polymer was reused up to 20 times and still converted more than 30% of the feed. In these recycling experiments, after each reaction the product was filtered off, the polymer was washed several times with methanol, and the new reaction was started by adding new olefin and fresh co-catalyst. The liquid phase, when separated from the polymer, showed very little catalytic activity, demonstrating that the reaction takes place in a truly heterogenized manner on the polymer itself.

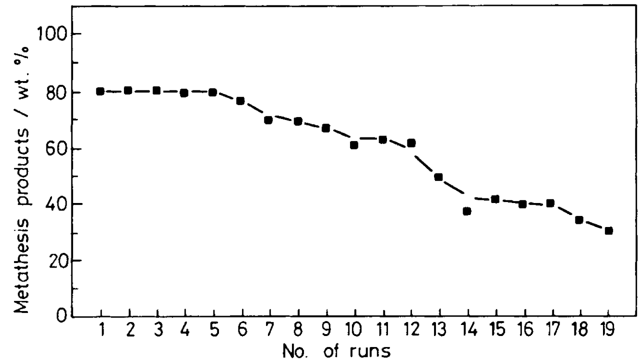

Figure 1. Recycling experiments using the polymer-bound catalyst component Ⓟ-CH_2–C_5H_4-η^5-W(CO)$_3$H

When this reaction sequence was followed by means of i.r. analysis, it was found that the original carbonyl stretching frequencies of the polymer-bound hydride complex at 2018 and 1920 cm^{-1} were gradually replaced by three new bands at 2040, 1958, and 1940 cm^{-1}. A comparison with literature data strongly suggested that these bands belong to the polymer-bonded analogue of (η-C_5H_5)W(CO)$_3$Cl. (η-C_5H_5)W(CO)$_3$Cl is obtainable by stirring (η-C_5H_5)W(CO)$_3$H in CCl_4.[2] Simi-

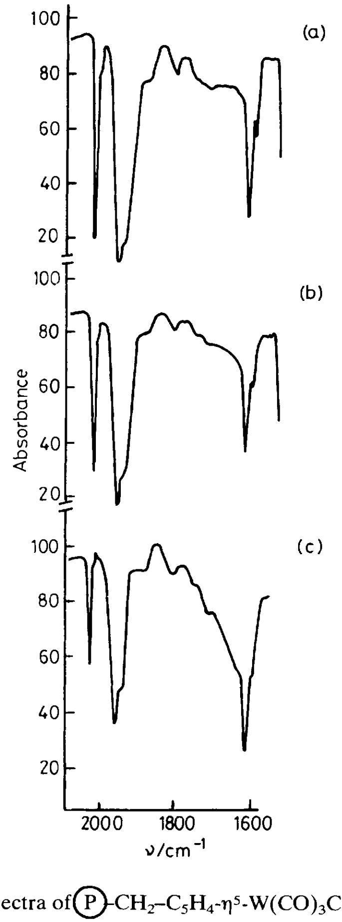

Figure 2. I.r. spectra of Ⓟ-CH_2–C_5H_4-η^5-W(CO)$_3$Cl in the carbonyl stretching region, (a) fresh complex, (b) recovered once, (c) recovered 15 times.

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larly, the polymer-supported form of the hydride complex reacted with CCl_4 to form a new complex, which indeed showed the new CO absorptions observed earlier. This complex, when employed for the metathesis of hept-3-ene, could be recovered unchanged after each reaction (Figure 2). It is therefore the chloro compound Ⓟ–CH_2–C_5H_4-η^5-$W(CO)_3Cl$ that is repeatedly recoverable for the metathesis reaction, and this complex can either be used as it is or be formed *in situ* from the hydrido complex. It should be noted that in Figure 2 there is a decrease in the CO bands compared with the polystyrene band at 1600 cm^{-1}. This observation is in agreement with the measured tungsten losses (5.86% on the fresh polymer, 3.06% after 15 runs) and with the decrease in activity reflected in the decrease in conversion from 80.9 to 44.0%.

The results presented make it likely that the olefin metathesis reaction proceeds with complexes of the type $(\eta$-$C_5H_5)W(CO)_3R$ under maintenance of the structural unit $(C_5H_5)W(CO)_3$ with R being a labile ligand. The factors contributing to the high stability of $(\eta^5$-$C_5H_5)M(CO)_3$ systems are well known.[3] That the reaction is indeed initiated by abstraction of the ligand R from $(\eta^5$-$C_5H_5)W(CO)_3$ by the aluminium–organic co-catalyst, thereby creating a vacant co-ordination site for the incoming olefin, is further confirmed by the fact that the reaction rate depends on the quality of R^- as a leaving group. When three complexes Ⓟ–CH_2–C_5H_4-η^5-$W(CO)_3R$ with R = Me, H, or Cl are employed under the same conditions, they show during their first use the following order of reactivity: $CH_3 < H \simeq Cl$.

The results reported therefore suggest that any proposal for the catalytic cycle should take into consideration that the cyclopentadienyl and the three carbonyl ligands are to be accommodated in the catalytically active complex. The mechanistic implications entailed will be discussed in a later paper.

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