

Olefin Metathesis. Development of a New Catalyst employing Tungsten Hexachloride and Lithium Aluminium Hydride

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Lithium aluminium hydride is an effective co-catalyst with tungsten hexachloride for metathesis of olefins. Optimum conditions for employment of the catalyst have been established and the observation of an induction period following addition of olefin has been interpreted in terms of an initial activation of the catalyst system.

FOLLOWING the discovery¹ of olefin metathesis (disproportionation) in 1964, a wide variety of heterogeneous catalysts for this process was developed.² Interest in the metathesis reaction as a potential laboratory-scale synthetic procedure was stimulated by reports³ of homogeneous catalysts which would effect disproportionation in solution at room temperature and atmospheric pressure in a few seconds or minutes. These catalysts have generally consisted of a combination of a Group 6 or 7 transition-metal compound and an alkyl derivative of aluminium,^{3,4} lithium,⁵ tin,⁶ or magnesium.⁷ The reactivity and air-sensitivity of these metal alkyls encouraged a search for an alternative catalyst system.

A brief report⁸ has been made on the use of lithium aluminium hydride as an effective co-catalyst with tungsten hexachloride for olefin metathesis. This system has the merits of ready availability and relative stability to air. Subsequent to submission of this report, Chatt *et al.*⁹ independently found that both

lithium aluminium hydride and sodium borohydride will serve as co-catalysts with tungsten hexachloride for olefin metathesis. More recently, Rossi and Giorgi¹⁰ described the application of WCl_6 - $LiAlH_4$ for the metathetical polymerisation of (*Z,Z*)-cyclonona-1,5-diene, which led to 'unexpected' results. Hydrides of silicon have also been employed as co-catalysts¹¹ and there has been much speculation recently concerning the precise role of hydride reducing agents in the metathesis reaction.^{11,12} In the light of this interest and also in view of conflicting statements concerning catalyst levels, ratios, and induction periods to be found in reports relating to the use of WCl_6 - $LiAlH_4$, we now describe in detail our studies of this catalyst system.

RESULTS AND DISCUSSION

In a series of reactions, the metathesis of hept-3-ene with WCl_6 and $LiAlH_4$ was followed by quantitative

⁷ (a) P. A. Raven and E. J. Wharton, *Chem. and Ind.*, 1972, 292; (b) T. Takagi, T. Hamaguchi, K. Fukuzumi, and M. Aoyama, *J.C.S. Chem. Comm.*, 1972, 838.

⁸ S. A. Matlin and P. G. Sammes, *J.C.S. Chem. Comm.*, 1973, 174.

⁹ J. Chatt, R. J. Haines, and G. J. Leigh, *J.C.S. Chem. Comm.*, 1972, 1202.

¹⁰ R. Rossi and R. Giorgi, *Tetrahedron Letters*, 1976, 1721.

¹¹ (a) J. Levisalles, H. Rudler, and D. Villemain, *J. Organometallic Chem.*, 1975, **87**, C7; (b) N. S. Nemetkin, V. M. Vdovin, E. D. Babich, V. N. Karelskii, and B. V. Kacharmin, *Doklady Akad. Nauk S.S.S.R.*, 1973, **213**, 356.

¹² R. J. Jaines and G. J. Leigh, *Chem. Soc. Rev.*, 1975, **4**, 155.

¹ G. C. Bailey and R. L. Banks, *Ind. Eng. Chem. (Product Res. and Development)*, 1964, **3**, 170.

² G. C. Bailey, *Catalysis Rev.*, 1969, **3**, 37.

³ (a) N. Calderon, M. Y. Chen, and K. W. Scott, *Tetrahedron Letters*, 1967, 3327; (b) N. Calderon, W. A. Judy, E. A. Ofstead, and K. W. Scott, *J. Amer. Chem. Soc.*, 1968, **90**, 4133.

⁴ G. Doyle and W. R. Kroll, *Chem. Comm.*, 1971, 839.

⁵ H. R. Menapace and J. L. Wang, *J. Org. Chem.*, 1968, **33**, 3794.

⁶ C. Boelhouwer and J. A. Mouljijn, *Chem. Comm.*, 1971, 1170.

g.l.c. Chlorobenzene was selected as solvent, since it has a convenient g.l.c. retention time and also avoids the

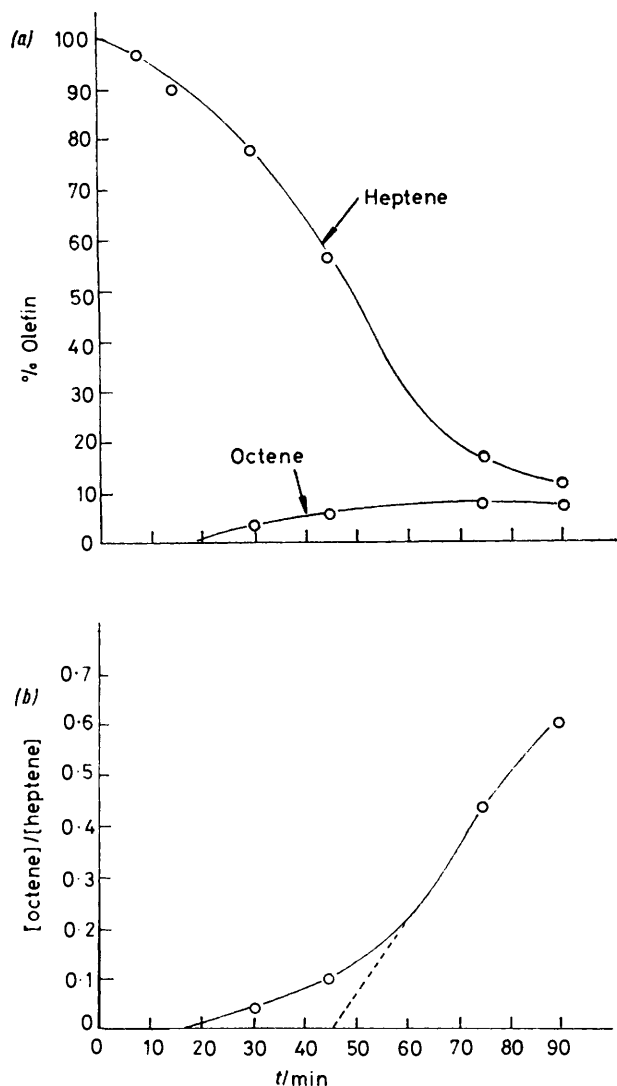
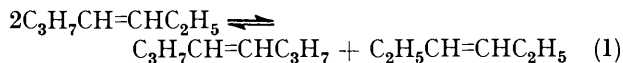


FIGURE 1 W : Al : Olefin 1 : 4 : 20; olefin concentration 2 mol per litre of solvent

problem of competing alkylation reactions¹³ associated with the use of benzene. Previous workers also used chlorobenzene.^{9,10}

In the first set of experiments, a solution of hept-3-ene in chlorobenzene (2 mol olefin per litre of solvent) was treated at room temperature with a mixture of WCl_6 and LiAlH_4 , the W : olefin ratio being maintained at 1 : 20 and the W : Al ratio varied from 1 : 1 to 1 : 6. In each case, samples were removed at intervals and examined by g.l.c. The overall metathesis reaction is expected

to approach the equilibrium depicted in equation (1).



These graphs indicate that the concentration of hept-3-ene begins to fall from the moment of mixing of the reagents whereas formation of oct-4-ene does not begin for some time. Thus, there is an induction period, and it appears that under these conditions 10–50% of the hept-3-ene is consumed in activating the catalyst. An estimate of the length of the induction period was made by projecting the straight, central portion of the [octene]/[heptene] vs. t graph [Figure 1(b)] back onto the time axis. Using the times obtained in this way for the whole series of experiments it was found that the induction period decreases in a roughly linear manner as the Al : W ratio is increased (Figure 2). Chatt *et al.* also noted an induction period following addition of the olefin, and both they⁹ and Rossi and Giorgi¹⁰ recommended pre-mixing of the LiAlH_4 and WCl_6 before addition of the olefin in order to shorten further the reaction time.

The absolute concentration of oct-4-ene reaches a maximum and then declines. The concentration of hept-3-ene similarly continues to decline throughout the reaction, whilst the octene : heptene ratio tends towards a maximum. Thus, there is at least one secondary reaction occurring in addition to metathesis which gradually removes all olefins from solution.

In each run of the series, the gradient of the graph of [oct-4-ene]/[hept-3-ene] against time at the point where the metathesis had proceeded to half the theoretical limit ([oct-4-ene]/[hept-3-ene] = 0.25) was taken as a measure of the rate of metathesis. A plot of this value for each run against the Al : W ratio used shows that the

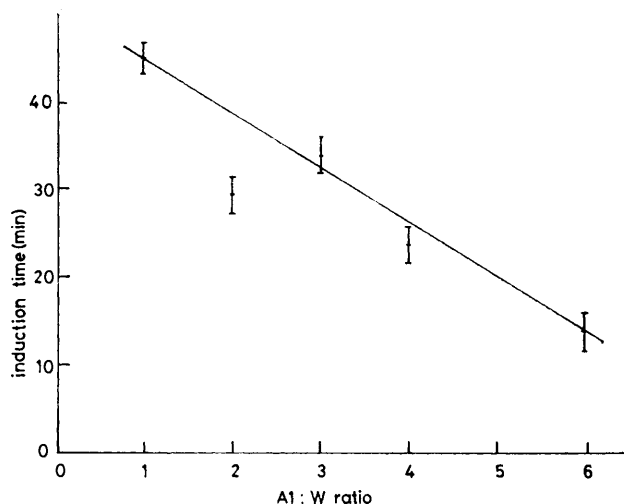


FIGURE 2 Induction time vs. Al : W ratio

¹³ (a) J. R. Graham and L. H. Slaugh *Tetrahedron Letters*, 1971, 787; (b) V. M. Kothari and J. J. Tazuma, *J. Org. Chem.*, 1971, **36**, 2951; (c) L. Hocks, A. J. Hubert, and P. Teyssie, *Tetrahedron Letters*, 1974, 877.

optimum Al : W ratio is 4 : 1 (Figure 3). Calderon has also reported that an Al : W ratio of 4 : 1 is the most effective with the $\text{WCl}_6\text{-AlEtCl}_2$ catalyst.^{3b} Rossi and

Giorgi¹⁰ also found an Al : W ratio of 4 : 1 to be optimum for the metathetical polymerisation of cycloalkenes; Chatt *et al.*⁹ used an excess of LiAlH₄.

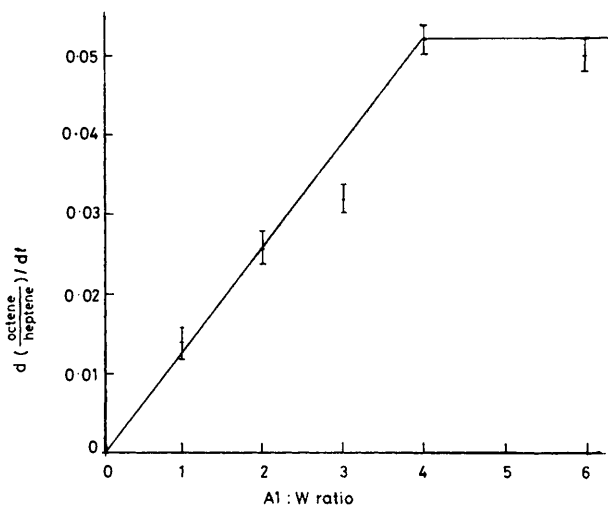


FIGURE 3 Metathesis rate vs. Al : W ratio

Under the optimum conditions derived above (W : Al : olefin 1 : 4 : 20; concentration of olefin 2 mol per litre of solvent) the yield of oct-4-ene was about 35% of theoretical.

A further series of variations was then carried out to maximise the yield. Increasing the olefin : W ratio while keeping the olefin concentration constant greatly increased the induction time and increased the yield of oct-4-ene. For an olefin : W ratio of 50 : 1 (Figure 4) the yield was 70% of theoretical, but at higher ratios the reaction became increasingly sluggish and failed to reach completion, probably owing to catalyst decomposition (indicated by the formation of a copious grey-green precipitate over 2–3 h). Keeping the olefin : W : Al ratio constant (20 : 1 : 4) and lowering the olefin concentration increased the induction period considerably, whilst the yield of oct-4-ene dropped to 30% of theoretical (Figure 5). Thus, increases in both the olefin : W ratio and olefin concentration improved metathesis efficiency up to a W : Al : olefin ratio of 1 : 4 : 100 and an olefin concentration of 5 mol per litre of solvent, when the yield of oct-4-ene was 75%. With further increases in olefin concentration (to 10 mol per litre of solvent) the rate of metathesis began to decrease and large amounts of by-products were observed, some of which appeared to result from metathesis of isomers of the starting material. This is consistent with the report¹⁰ of isomerisations during the metathesis of cyclononadiene.

Finally, the best results achieved were those in which a W : Al : olefin ratio of 1 : 4 : 80 and olefin concentration of 6 mol per litre of solvent were employed (Figure 6). A mixture of 18.5% hexene (*i.e.* 74% of theory), 39.8% heptene (79.6% of theory), and 23.4%

octene (93.6% of theory) was produced in 130 min, as well as a mixture of three other products (*ca.* 10% total) indicated by their g.l.c. retention times to be butene, pentene, and nonene. The reaction under these conditions was successful on a preparative scale, with 20 g (0.2 mol) of hept-3-ene.

Any interpretation of the role of LiAlH₄ in the metathesis reaction must be able to account for the observed induction period, and for the eventually complete consumption of both reactant and product olefins at

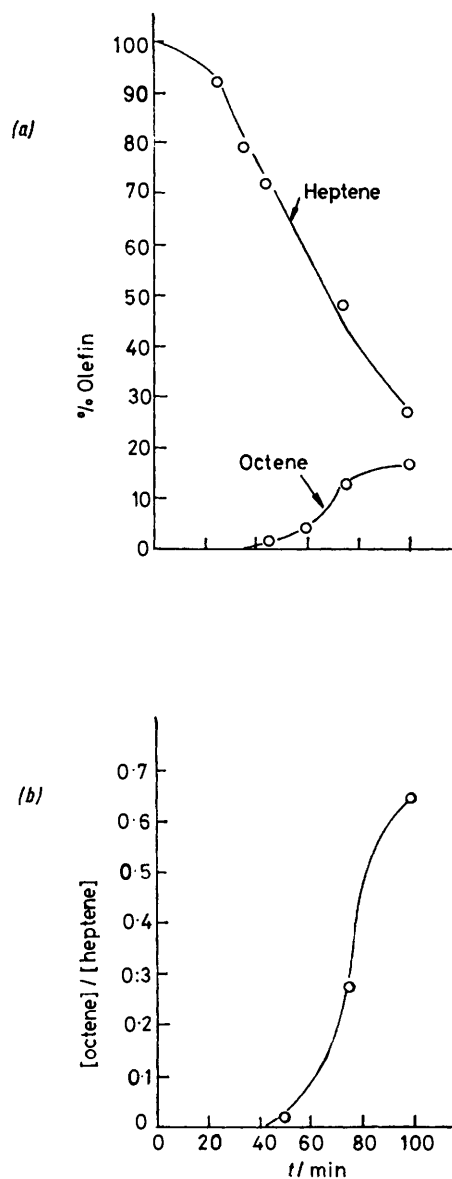


FIGURE 4 W : Al : Olefin 1 : 4 : 50; olefin concentration 2 mol per litre of solvent

high catalyst concentrations, and must be consistent with the other known facts about the reaction.

Tetrahydroaluminate ion is known to react with

olefins by addition, producing trihydroalkylaluminum ions [equation (2)]. The reaction is most favourable for

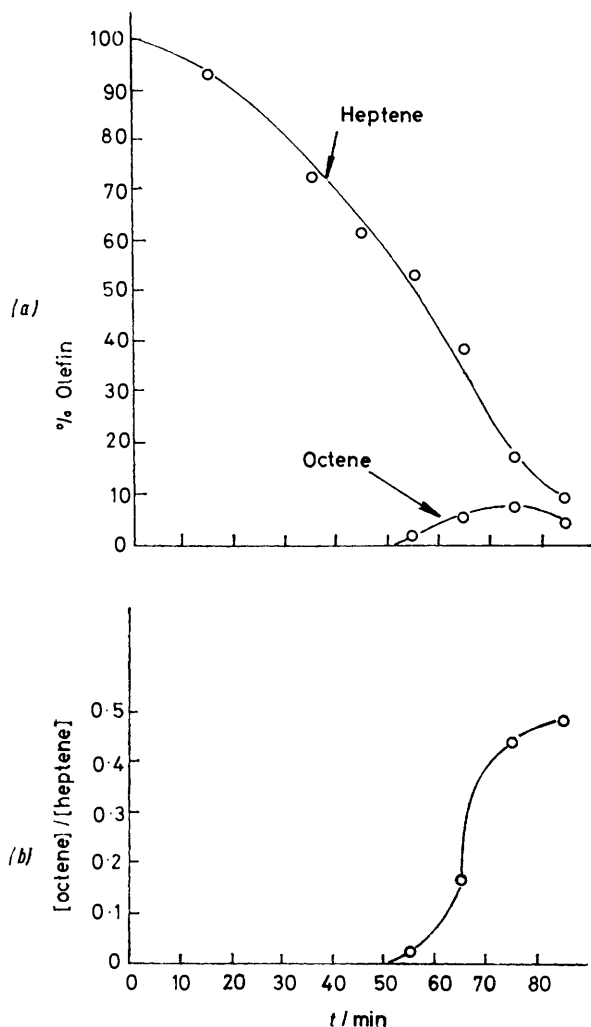
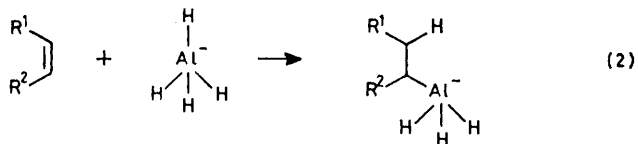


FIGURE 5 W : Al : Olefin 1 : 4 : 20; olefin concentration 0.5 mol per litre of solvent

terminal olefins,¹⁴ but is known to be catalysed by the salts of transition metals.¹⁵ It is possible, therefore, that an aluminium alkyl is formed, which reacts further with WCl_6 to generate the active catalyst. This would account for the induction period and for the initial con-



sumption of hept-3-ene. Furthermore, $LiAlH_4$ has been reported¹⁶ to isomerise internal to terminal olefins

¹⁴ H. G. Gellert, H. Martin, K. Nagel, J. Schneider, and K. Ziegler, *Annalen*, 1954, **589**, 91.

during the formation of alanes, which could account for the isomerisations noted when it is used as a metathesis co-catalyst. However, the extent of metal alkyl formation must be relatively small, since after quenching reaction mixtures with methanol little or no by-product is observed on g.l.c. which might be attributed to hydrocarbon formation. The eventual consumption of all olefins present when high catalyst levels are used

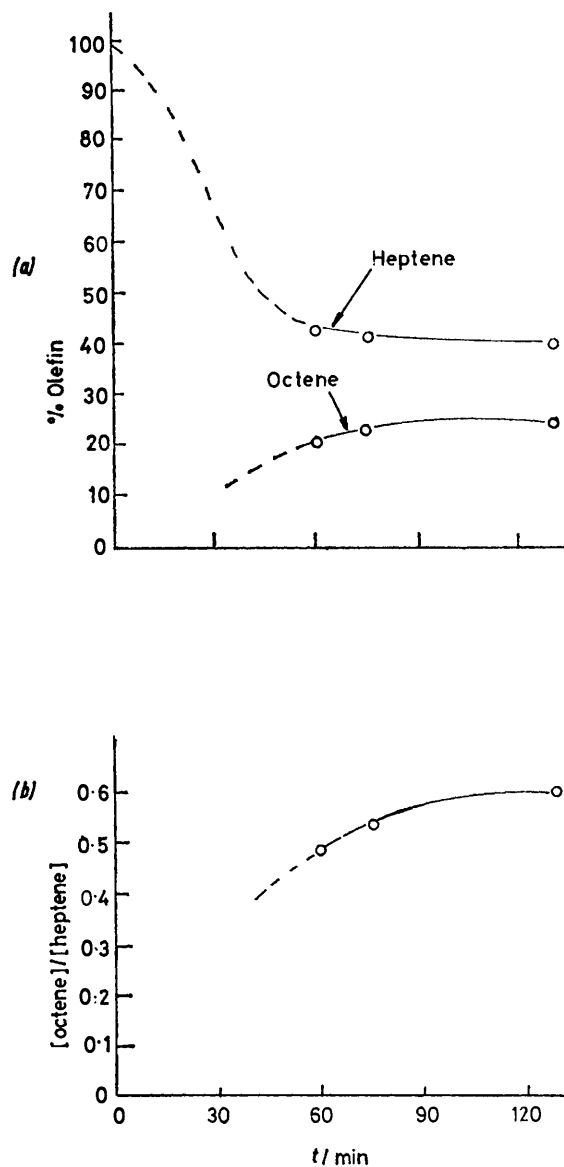


FIGURE 6 W : Al : Olefin 1 : 4 : 80; olefin concentration 6 mol per litre of solvent

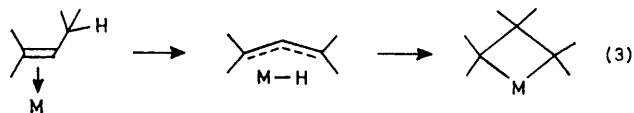
may be the result of interaction of metal alkyls with the alkenes, leading to products of high molecular weight.

¹⁵ F. Asinger, B. Fell, and R. Janssen, *Chem. Ber.*, 1964, **97**, 2515.

¹⁶ P. Binger and R. Koster, *Adv. Inorg. Chem. Radiochem.*, 1965, **7**, 263.

The alternative, of alkylation of the solvent, is considered unlikely. No alkylation of chlorinated aromatic hydrocarbon solvents under metathesis conditions has been observed with this⁹ or other^{13c,17} catalysts, whereas the observation of oligomerisation accompanying metathesis is not uncommon.¹²

LiAlH_4 may also act as a reducing agent for tungsten hexachloride. The reduction of the latter to WCl_4 by silanes, which will also function as metathesis co-catalysts, has been reported.¹¹ However, WCl_4 is not, on its own, an active catalyst for disproportionation.¹⁸ The involvement of tungsten hydrides in metathesis has been proposed by Levisalles *et al.*,^{11a} both when hydrides of Al, B, and Si are used and also with the conventional metal alkyl co-catalysts. Green *et al.*¹⁹ have recently shown that π -alkyltungsten complexes will rearrange on attack by hydride ion to give metallacyclobutanes. π -Alkyltungsten hydride complexes can also be formed by β -hydrogen migration to the metal in tungsten-olefin complexes, leading to the proposal of the mechanism shown in equation (3) for the formation of a metalla-



cyclobutane. There is now a considerable body of evidence²⁰ to suggest that metallacyclobutanes are intermediates in metathesis, reversibly decomposing to an olefin and a tungsten-carbene complex. A further role for the LiAlH_4 may be to furnish chloroaluminium species by reaction with WCl_6 , such species by virtue of their Lewis-acid character helping to stabilise the intermediate tungsten-carbene complexes subsequently generated.²¹

¹⁷ Y. Uchida, M. Hidai, and T. Tatsumi, *Bull. Chem. Soc. Japan*, 1972, **45**, 1156.

¹⁸ N. Calderon, *Accounts Chem. Res.*, 1972, **5**, 127.

¹⁹ M. Ephritikhine, M. L. H. Green, and R. E. MacKenzie, *J.C.S. Chem. Comm.*, 1976, 619.

EXPERIMENTAL

Commercial tungsten hexachloride was purified^{3b} by heating for 1 h at 200–220 °C in a stream of pure nitrogen; orange vapours of WCl_4O and yellow vapours of WCl_2O_2 sublimed off, leaving pure, blue WCl_6 which was stored under nitrogen over P_2O_5 . Chlorobenzene was distilled from P_2O_5 or sodium-lead alloy and stored over sodium-lead alloy under nitrogen. Commercial hept-3-ene was fractionally distilled from P_2O_5 through a 9 in Vigreux column (b.p. 96 °C at 772 mmHg), stored over P_2O_5 , and filtered through grade I alumina immediately before use. G.l.c. analyses were performed on a Perkin-Elmer F11 dual-column flame ionisation chromatograph fitted with two glass columns (6 ft \times 1/4 in o.d.; 15% squalane on Chromosorb P, 80–100 mesh).

General Metathesis Procedure.—Reactions were conducted in a 25 ml cylindrical, flat-bottomed flask fitted with nitrogen inlet and outlet tubes and a rubber septum. After introduction of the solid catalyst components and a magnetic stirrer, the flask was flushed with dry, oxygen-free nitrogen for at least 15 min before addition of chlorobenzene and hept-3-ene by graduated syringe and commencement of stirring. Samples (0.1–0.2 ml) were removed at intervals by syringe and immediately injected into sealed 5 ml flasks containing methanol (0.2 ml), the sample flasks being cooled in acetone–solid CO_2 immediately before a g.l.c. sample was taken with a microsyringe. The bulk reaction was terminated at the desired time by injection of methanol (0.25 ml). Time-course experiments were generally performed on 0.01 mol of hept-3-ene.

Preparative-scale Metathesis of Hept-3-ene.—To WCl_6 (0.991 g, 0.0025 mol) and LiAlH_4 (0.382 g, 0.010 mol) under nitrogen in a 100 ml flask was added hept-3-ene (20.00 g, 0.204 mol) in chlorobenzene (33.4 ml). The mixture was stirred for 130 min and reaction terminated by addition of methanol (1.5 mg). G.l.c. analysis showed hexene (14%), heptene (38%), and octene (20%) to be present.

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²⁰ T. J. Katz and R. Rothchild, *J. Amer. Chem. Soc.*, 1976, **98**, 2519; R. H. Grubbs, D. D. Carr, C. Hoppin, and P. L. Burk, *ibid.*, p. 3478; P. G. Gassman and T. H. Johnson, *ibid.*, pp. 6055, 6057, 6058; N. Calderon, E. A. Ofstead, and W. A. Judy, *Angew. Chem. Internat. Edn.*, 1976, **15**, 401.

²¹ E. L. Muetterties, *Inorg. Chem.*, 1975, **14**, 951.