

³¹P Nuclear Magnetic Resonance and Infrared Spectroscopic Evidence for Co-ordinatively Unsaturated Zerovalent Tungsten Generated by Interaction of W(CO)₅L (L = PPh₃ or PBuⁿ₃) with AlBr₃

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Summary With the metathesis catalyst W(CO)₅L·AlBr₃, AlBr₃ acts first as a Lewis acid to give a 1:1 adduct which further yields a co-ordinatively unsaturated, relatively stable zerovalent tungsten.

OLEFIN metathesis has been the subject of intense research in the last decade.¹ Although the 'one-carbene exchange' mechanism seems to be commonly accepted,² a great deal of uncertainty remains as to the mode of formation of the metallo-carbene necessary for the propagation step. It has been shown that, with co-catalysts having alkylating properties such as ZnMe₂³ or SnMe₄⁴ or any organo-aluminium compound such as R_xAlCl_{3-x} (*x* ≠ 0)⁵ associated with various types of Mo, W, or Re complexes, the product distribution obtained in the early stages of the catalytic reaction is best described as being the result of a metathesis reaction with a metallo-carbene resulting from the alkylation of tungsten (followed by an α-elimination of hydrogen).⁶ However such a possibility does not apply to typical Lewis acids such as AlCl₃ or AlBr₃ which are usually much better co-catalysts of low-valent tungsten complexes than typical alkylating agents. In order to shed additional light on the role of the co-catalyst in metathesis, we have investigated by ³¹P n.m.r. and i.r. spectroscopy the interaction between W(CO)₅L (L = PPh₃ or PBuⁿ₃) and AlBr₃ in chlorobenzene. This catalytic system has proved to be very active in metathesis of acyclic and cyclic olefins.⁷

Complex W(CO)₅L (L = PPh₃ or PBuⁿ₃) in chlorobenzene solution exhibits two ν(CO) vibrations (*A*₁¹, *A*₁², and *E* modes corresponding to the *C*_{4v} symmetry; the *A*₁¹ and *E* modes are accidentally degenerate)⁸ (Table). With proton noise decoupling, the ³¹P n.m.r. spectrum (at 40.5 MHz) of W(CO)₅PPh₃ consists of a sharp central peak at δ -19.7 p.p.m. (down-field from external H₃PO₄) flanked by two satellites due to the coupling to ¹⁸³W (*I* = ½, 14.42% natural abundance) (*J*_{P-W} = 244 Hz) (Figure, a) in fair agreement with earlier work.⁹

In the early stages following addition of an excess of AlBr₃ to a 5 × 10⁻³ M solution of W(CO)₅PPh₃, the phosphorus resonance moves to higher field (δ -11.2 p.p.m. from H₃PO₄) while the *J*_{P-W} remains observable and unchanged. In the i.r. spectrum the *A*₁¹ mode is shifted to lower frequencies by 272 cm⁻¹ giving rise to a broad ν(CO) band while the *E* mode is shifted to higher frequency, the value of which depends on the nature of the phosphine (Table); in contrast the *A*₁² mode is no longer observed

TABLE. ν(CO) vibrations (in cm⁻¹) of the intermediate compounds resulting from the interaction of W(CO)₅L with AlBr₃ in chlorobenzene solution.

Ligand (L)	Starting compound	Inter-mediate (I)	Inter-mediate (II)
PPh ₃	2068w, 1937s	1996s, 1665s	2013s, 1630s
PBu ⁿ ₃	2064w, 1930s	1991s, 1665s	2013s, 1630s

probably owing to its weak extinction coefficient. Progressively the i.r. spectrum is slightly modified with a further shift to higher frequencies and the corresponding i.r. spectrum is independent of the nature of the phosphine (Table). The ^{31}P n.m.r. spectrum shows a new peak at $\delta -5.8$ p.p.m. No splitting of the singlet by the ^{183}W nucleus is observed indicating that the phosphine is no longer co-ordinated to tungsten. The intensity of this singlet increases at the expense of that of the triplet at $\delta -11.2$ p.p.m. (Figure).

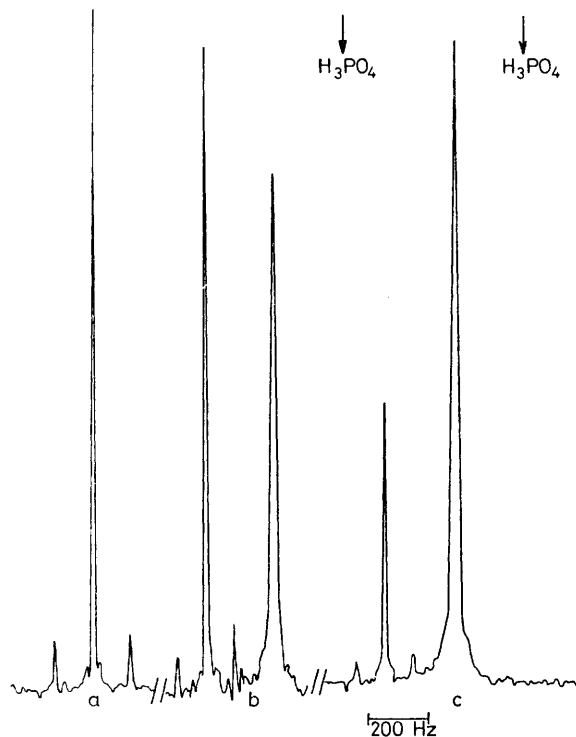


FIGURE. F.T. ^{31}P n.m.r. spectra at 40.5 MHz under proton noise decoupling and using a fluorine external lock: (a) $\text{W}(\text{CO})_5\text{PPh}_3$ in PhCl , (b) $\text{W}(\text{CO})_5\text{PPh}_3 + \text{AlBr}_3$ (excess), and (c) same as (b) after 3 h (frequency scale shifted).

The position of both signals varies with the Al:W ratio; as the Al:W ratio is increased, the triplet moves upfield and the singlet moves downfield relative to $\text{W}(\text{CO})_5\text{PPh}_3$ and free phosphine signals, respectively. Under similar conditions (Al:W < 1:1) all species described previously could be observed simultaneously by i.r. spectroscopy.

The ^1H decoupled ^{31}P n.m.r. spectrum of PPh_3 in PhCl is a singlet at $\delta +6.2$ p.p.m. in agreement with the litera-

ture.¹⁰ Addition of AlBr_3 caused the phosphorus resonance to shift progressively to lower fields and a value of $\delta -5.8$ p.p.m. is achieved for the ratio Al:W = 20:1.

Combination of i.r. and ^{31}P n.m.r. spectroscopy provides a convenient way to characterize the various species resulting from the interaction of $\text{W}(\text{CO})_5\text{L}$ and AlBr_3 . The i.r. spectrum shows that, in the early stages of the reaction, the C_{4v} symmetry of the starting complex remains intact. The ^{31}P n.m.r. spectrum indicates unambiguously, *via* the $\text{P}-^{183}\text{W}$ coupling, that the phosphine is still co-ordinated to the tungsten. Therefore this species is best described as a $\text{W}(\text{CO})_5\text{PPh}_3\text{AlBr}_3$ adduct where the aluminium is interacting with the CO ligand *trans* to PPh_3 *via* $\text{W}-\text{CO} \rightarrow \text{Al} \rightleftharpoons$ complexation¹¹ (shift of the A_1^1 mode to lower frequency and conservation of the symmetry). The dependence of the ^{31}P resonance position on the AlBr_3 concentration is characteristic of a dynamic equilibrium between the initial compound and the adduct.

In the next step, as shown by the i.r. spectrum, there is also a conservation of the initial C_{4v} symmetry. The invariance of the $\nu(\text{CO})$ frequency with respect to the nature of the phosphine ligand suggests that the species results from the previous one by deco-ordination of the phosphine ligand. This is proved by the ^{31}P n.m.r. spectrum indicating that (i) the phosphine is no longer interacting with the tungsten and (ii) the intensity of the ^{31}P signal increases at the expense of the signal due to the former species. Hence we are dealing with an adduct co-ordinatively unsaturated owing to the loss of the phosphine ligand. It is not unreasonable to assume that the free co-ordination site could be occupied by one molecule of solvent.

As to the fate of the leaving ligand, since the ^{31}P n.m.r. spectrum does not show a resonance corresponding to the free phosphine ligand one must assume that a dynamic equilibrium $\text{AlBr}_3 + \text{PPh}_3 \rightleftharpoons \text{Ph}_3\text{P} \rightarrow \text{AlBr}_3$ is prevailing. A fast exchange between the free phosphine and that complexed by the Lewis acid would result in the collapse of the two lines due to each of the species into a single line, the position of which is determined by the relative ratio of W to AlBr_3 . This is what is actually observed, which shows that the leaving phosphine is indeed interacting with the Lewis acid, thus preventing the re-co-ordination of the phosphine which should have an inhibiting effect in the catalytic process.

Besides the metathesis reaction, this pattern could be conceived as a general scheme for the activation of various precursor complexes by Lewis acids in homogeneous catalysis.

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