Tungsten(IV) Carbenes for the Metathesis of Olefins. Direct Observation and Identification of the Chain Carrying Carbene Complexes in a Highly Active Catalyst System

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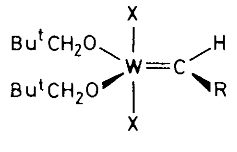
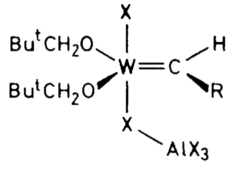
On addition of aluminium halides to the carbene complexes $W(CHBu^t)(OCH_2Bu^t)_2X_2$ conversion into highly active catalysts for olefin metathesis occurs; the nature of the initiating and propagating species in olefin metathesis has been identified by n.m.r. spectroscopy.

Tungsten carbene species have long been implicated as catalytic intermediates in the olefin metathesis reaction[1] and recent elegant mechanistic[2] and model studies[3] have largely confirmed this supposition. We report (i) the isolation of simple carbene complexes of W^{IV} from a classical catalyst system, (ii) the nature of their interaction with Lewis acids, (iii) the high activity of these complexes as metathesis catalysts, and (iv) the *direct* observation and identification of the chain carrying carbene intermediates *during* olefin metathesis.

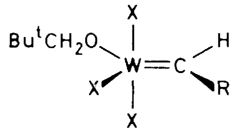
We have previously reported[4] the interaction of $WO(OCH_2Bu^t)_2(CH_2R)_2$ ($R = Bu^t$) with Lewis acids AX_n (*e.g.* AlX_3; $X = Cl, Br$) to yield the adducts $W(OAX_n)(OCH_2Bu^t)_2(CH_2R)_2$. We find now that these species slowly transform in solution (CH_2Cl_2) to form the carbene complexes $W(CHR)(OCH_2Bu^t)_2X_2$, $(AlOX)_n$, and RCH_3. These surprisingly simple metal carbene complexes are relatively stable *e.g.* $W(CHR)(OCH_2Bu^t)_2Br_2$ can be sublimed (60 °C, 10^{-4} mmHg) as a pale yellow powder, which melts at -5 °C to an orange



(1)



(2)



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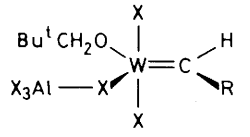

(4)

Table 1. Selected spectroscopic data for (1)—(4) (X = Br,[a] -30 °C).

		(1)	(2)	(3)	(4)
$^1H(\delta)$	(C_6D_5Cl)				
	W=C*H*Bu^t	11.17	12.09	8.48	10.20
	W(OC*H*$_2$Bu^t)	4.43 4.41	4.50	4.22	4.50
$^{13}C(\delta$/p.p.m.)	(CD_2Cl_2)				
	W=*C*HBu^t	298.6	314.9	308.2	322.1
	(J(C–H)/Hz)	(138)	(138)	(127)	(127)
	W(O*C*H$_2$Bu^t)	91.8 90.4	91.4 91.2	99.0	97.9

[a] For X = Cl, ^1H n.m.r.: δ 10.80 (W=C*H*Bu^t); ^{13}C n.m.r.: δ 291.7 p.p.m. (W=*C*HBu^t).

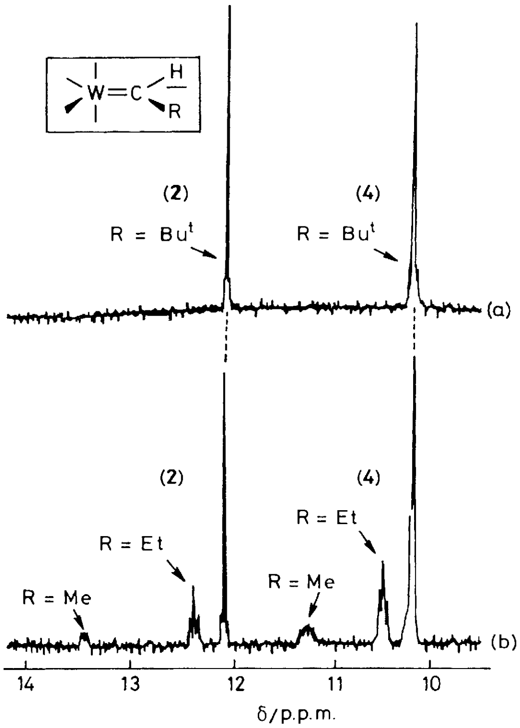

Figure 1. ^1H N.m.r. spectrum (W=C*H*R) measured at -30 °C in C_6D_5Cl of (a) the *ca.* 1:1 mixture of (2) and (4) produced by treatment of (1) with $AlBr_3$ (3 mol), warming to -10 °C for 30 s, and then recooling to -30 °C, (b) after addition of *cis* MeCH=CHEt (10 mol) at -30 °C, warming to -10 °C for 30 s, and recooling to -30 °C.

oil. The ^1H and ^{13}C n.m.r. data (Table 1) along with the presence of a single i.r.-active W–X vibration (*e.g.* at 220 cm^{-1} for X = Br) lead us to propose structure (1) for these complexes.

These carbene complexes do not react with *cis*-pent-2-ene at 25 °C. However, addition of $AlBr_3$ (1 mol. equiv.) in PhCl produces an exceedingly active system which converts 10^3 mol. equiv. of *cis*-pent-2-ene into but-2-enes (*cis*: *trans* = 1:1) and hex-3-enes in less than 1 min. The use of $GaBr_3$ produces a similarly efficient catalyst whose lifetime exceeds 24 h.

The nature of the initiating and propagating species in these systems has been established by n.m.r. spectroscopy (^1H and ^{13}C) in C_6D_5Cl or CD_2Cl_2 at -30 °C. W(CHBu^t)(OCH$_2$Bu^t)$_2$Br$_2$ rapidly forms a strong 1:1 adduct with $AlBr_3$ at -30 °C in C_6D_5Cl in which the ^1H resonance of W=C*H*R is shifted to δ 12.09 from δ 11.17; an analogous shift of the ^{13}C resonance from 298.6 to 314.9 p.p.m. is also observed (in CD_2Cl_2). Notably however, complexation causes (i) no change in $J(C_\alpha$–H) in the W(CHR) moiety nor (ii) a significant displacement of the $-OCH_2R$ resonances in the ^1H or ^{13}C n.m.r. spectra. Hence structure (2) is indicated for these complexes, where $AlBr_3$ is bound conventionally to a halide ligand and not to the carbene.[3c,d] On warming this solution to -10 °C, (2) begins to be converted into W(CHBu^t)(OCH$_2$Bu^t)Br$_3$ (3) with formation of AlBr$_2$(OCH$_2$Bu^t). Pure (3) can be best produced by reaction of BBr_3 with (1) at -50 °C, and is less stable than (1) decomposing at *ca.* -5 °C. Complex (3) also forms a 1:1 complex with $AlBr_3$ (Figure 1a) for which structure (4) analogous to (2), is proposed from spectroscopic data (Table 1).

Addition of *cis*-MeCH=CHEt (*ca.* 10 mol) to a mixture of (2) and (4), warming to -10 °C for 30 s, and remeasuring the spectrum at -30 °C yielded the spectrum shown in Figure 1b. Four new carbene resonances have appeared, the original carbenes (2) and (4) (R = Bu^t) having decreased in intensity. The two carbenes at δ 12.40 [t, ^2J(H–H) 8 Hz] and 13.40 (br. quart.) correspond, respectively, to the formation of the moieties W=CHEt and W=CHMe of structure (2). The two other resonances at δ 10.55 (t) and 11.35 (br.) correspond to the analogous carbenes in the structural series (4); the relative intensities W(CHEt): W(CHMe) = *ca.* 4:1 are observed in both cases. Analysis by g.c./m.s. of these solutions showed the presence of both products of initiation, [Bu^{t}CH=CHMe and Bu^{t}CH=CHEt (ratio 1:1)], and metathesis, but-2-ene and hex-3-ene. If, alternatively, the olefin MeCH=CHPr^i is used in the same experiment, the doublets of W=CHPr^i appear at δ 12.35 (2) and 10.50 (4) as well as the broad quartets at δ 13.40 (2) and 11.35 (4) (relative intensities *ca.* 6:1).

Hence the *chain carrying carbene complexes* in their standing concentrations are observed in this highly active system and structures (2) and (4) assigned to these intermediates in which the binding of the Lewis acid is necessary for both initiation and propagation. Further, we note that (i) (4) is more active as a catalyst than (2) since the chain carrying carbenes of (4) appear before those of (2), (ii) the reactivities of the carbenes W=CHR of (2) and (4) with olefins follow the order R = Me > Et > Pr^i with an approximate reactivity ratio in the propagation cycle of 6:1.5:1, (iii) no intermediate olefin–carbene complex is detectable although in the presence of olefin the carbenes are less prone to decomposition, and (iv) the broad nature of the W(C*H*Me) resonance at -30 °C results from a dynamic exchange process which at -50 °C is sufficiently slow to show a resolved quartet for this resonance.

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