Tungsten(VI) and Molybdenum(VI) Oxo-alkyl Species. Their Role in the Metathesis of Olefins

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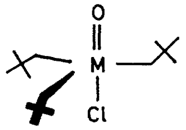
Summary The complexes MOCl (neopentyl)$_3$ (M = Mo, W) can be isolated from solutions which are active in olefin metathesis, and although inactive alone, these species can be converted into very active catalysts; the syntheses of MO(neopentyl)$_4$ (M = Mo, W) are also reported.

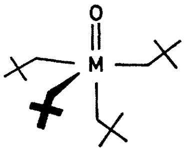
ALTHOUGH many studies on the metal-catalysed metathesis of olefins have implicated a metallo-carbene species as the reactive intermediate,[1] the detailed description of this species (*e.g.* oxidation state of the metal, ligand environment) and the role of the cocatalyst remain unclear for the most active systems. In a direct study of the solutions of the most reactive catalysts we have found[2] (as others)[3] that the presence of oxo-ligands on the metal [*e.g. via* impurities or the presence (deliberate or otherwise) of molecular oxygen][4] has a dramatic effect on catalytic activity. We report here a study of the reaction of $WOCl_4$ with dineopentylmagnesium and the species isolated therefrom.

$WOCl_4$ in ether reacted with 1 mol. equiv. of dineopentylmagnesium·dioxan to yield a deep brown solution and a precipitate of $MgCl_2$·dioxan. Filtration, and removal of ether yielded a red-brown solid; the hexane-soluble fraction of this solid is extremely active in the metathesis of olefins, but the insoluble residue is inactive. Removal of hexane from the active solution, and sublimation (50 °C; 10^{-4} mmHg) of the resultant solid yielded WOCl (neopentyl)$_3$ (A) as pure white microcrystals.[†] The ^{1}H n.m.r. spectrum (C_6D_6) shows singlets at δ 1·3 (9H) and 2·6 (2H); ^{13}C (C_6D_6; δ/p.p.m. from Me_4Si) 32·5 (C*Me*$_3$), 36·9 (*C*Me$_3$), and 101·2 (W–*C*H$_2$–). The i.r. spectrum shows *inter alia* a sharp, intense $\nu_{W=O}$ absorption at 977 cm^{-1}. Further, the mass spectrum shows the parent ion at *m/e* 446 and the expected intensity and fragmentation patterns.

Using analogous methods starting with $MoOCl_4$, the complex (B), MoOCl(neopentyl)$_3$, can be isolated, which shows closely similar physical and spectroscopic properties[‡] to those of (A). We suggest the structures shown for these complexes.



(A) M = W
(B) M = Mo



(C) M = W
(D) M = Mo

If $WOCl_4$ is treated with 2 mol. equiv. of dineopentylmagnesium·dioxan and worked up in a similar fashion complex (C), WO(neopentyl)$_4$, can be obtained as an orange powder after sublimation (70 °C; 10^{-4} mmHg). The ^{1}H n.m.r. spectrum (C_6D_6) shows resonances at δ 1·5 (27H, C*Me*$_3$) and 2·0 (6H, WC*H*$_2$) for the equatorial neopentyl groups, and δ 1·1 (9H, C*Me*$_3$) and 3·8 (2H, WC*H*$_2$) for the axial group. Similarly the ^{13}C n.m.r. spectrum (C_6H_6; δ p.p.m. from Me_4Si), shows the equatorial neopentyl ligands at δ 33·2 (C*Me*$_3$), 35·1 (*C*Me$_3$), and 87·3 (W*C*H$_2$) and the axial group at δ 27·0 (C*Me*$_3$), 34·2 (*C*Me$_3$), and 81·0 (W*C*H$_2$). The $\nu_{W=O}$ vibration appears at 946 cm^{-1}. The molybdenum analogue (D), MoO(neopentyl)$_4$ has been characterised similarly,[§] although a major product from this reaction is

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[†] Satisfactory elemental analyses were obtained for (A)—(D).

[‡] N.m.r.: ^{1}H (C_6D_6) δ 1·2 (9H, C*Me*$_3$) and 3·35 (2H, MoC*H*$_2$); ^{13}C (C_6D_6, δ/p.p.m. from Me_4Si) 31·7 (C*Me*$_3$), 36·9 (*C*Me$_3$), and 95·2 (Mo-*C*H$_2$); i.r. $\nu_{Mo=O}$ 952 cm^{-1}; *m/e* 321 (M^+ − Cl).

[§] N.m.r.: ^{1}H (C_6D_6) δ 1·0 (9H, C*Me*$_3$), 1·4 (27H, C*Me*$_3$), 2·4 (6H, MoC*H*$_2$), and 3·8 (2H, MoC*H*$_2$); i.r. $\nu_{Mo=O}$ 922 cm^{-1}.

$[Mo(neo\text{-}pentyl)_3(CCMe_3)]_2$ previously described.[5] The mechanism of formation of this species is being investigated.[6]

Whereas (A) (or B) is not a catalyst for the metathesis of olefins, the impure solid from which (A) is sublimed and which contains 80—90% of (A) is extremely active. The other component is a yet uncharacterised tungsten complex. Two hypotheses seem possible; the latter species is either active alone or serves as a cocatalyst for (A). In support of the latter hypothesis we find that very active catalysts are produced when (A) is treated with $WOCl_4$. Hence a 2×10^{-3} M solution of (A) and $WOCl_4$ (10^{-3} M) in chlorobenzene at 25 °C metathesises *cis*-pent-2-ene into but-2-ene (*cis*: *trans* *ca.* 2:1) and hex-3-enes at an initial rate of *ca.* 20 moles of olefin per mole of (A) per minute.

Hence it is possible that the classical cocatalysts (alkylating agents of Mg, Al, Sn, *etc.*) in olefin metathesis serve to generate the optimum combination of W (or Mo) complexes and do not themselves play a role in the propagation step of metathesis.

We thank the Centre National de la Recherche Scientifique and the A.T.P. (Catalyse Homogène) for financial support.

(*Received, 6th November* 1979; *Com.* 1174.)

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