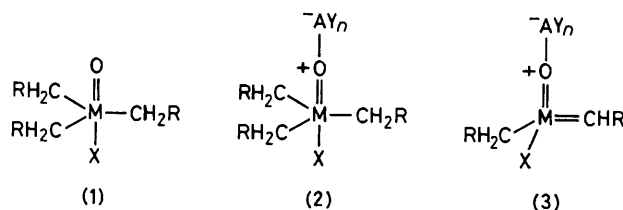


## Molecular Complexes for Efficient Metathesis of Olefins. The Oxo-ligand as a Catalyst-Cocatalyst Bridge and the Nature of the Active Species

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**Summary** Three families of molecular complexes for the homogeneous metathesis of olefins are described; the role of the oxo- or imido-ligand as bridge for binding the Lewis acid and the nature of the active species in metathesis are discussed.



M = Mo or W  
X = Cl, Br, or OR  
R = Bu<sup>t</sup>  
AY<sub>n</sub> = Lewis Acid

PREVIOUSLY<sup>1</sup> we have reported the preparation of complexes of type (1) and their conversion into active olefin metathesis catalysts by addition of WOCl<sub>4</sub>. We now find that complexes of type (1) and two other closely related series of complexes (5) and (6) interact very strongly with a variety of Lewis acids to produce well defined, extremely active molecular catalysts for olefin metathesis.<sup>2</sup>

Addition of 1 mol. equiv. of AlBr<sub>3</sub> to (1; X = Br) in hexane leads to the precipitation of the adduct (2) which can be recrystallised from toluene at -78 °C. The <sup>1</sup>H n.m.r. spectrum shows clean 1:1 adduct formation with notably a shift of the α-CH<sub>2</sub> resonances *ca.* 1 p.p.m. to lower field. Similar behaviour was found for BBr<sub>3</sub>, AlCl<sub>3</sub>, GaCl<sub>3</sub>, and SnCl<sub>4</sub> with (1; X = Cl, Br, or OR) (Table) and for MgBr<sub>2</sub> and ZnCl<sub>2</sub> with (1; X = OR). I.r. data in all cases showed the ν(W=O) to shift on complexation to lower frequencies [*e.g.* from 978 cm<sup>-1</sup> (X = Cl or Br) to 952 cm<sup>-1</sup> (with AlCl<sub>3</sub>) or 840 cm<sup>-1</sup> (with GaCl<sub>3</sub>)]<sup>†</sup> whereas ν(W-X) increased in frequency by +10–25 cm<sup>-1</sup>. Structure (2) is therefore proposed for this series of complexes<sup>‡</sup> where, importantly, the Lewis acid is bound to the oxo-ligand. Such complexes are very active, long-lived catalysts in solution; *e.g.* W(OAlBr<sub>3</sub>)Br(CH<sub>2</sub>R)<sub>3</sub> in PhCl under ambient conditions metathesises *cis*-pent-2-ene (500 mol. equiv.) at an initial rate of *ca.* 60 mol min<sup>-1</sup>.

However only those adducts (2) which release neopentane in solution (however slowly) are active catalysts. Importantly we find that neopentane release occurs photochemically (ambient neon or sun light) and hence catalytic activity is photoinitiated. The transformation of (2) to (3) is thus indicated as the initiation step in the metathesis using these catalysts. The proposition that the Lewis acid AY<sub>n</sub> continues to co-ordinate to the carbene complex [as in (3)] is supported by two lines of evidence. (a) In the metathesis of *cis*-pent-2-ene, the *initial cis/trans* ratio of the but-2-ene product varies with AY<sub>n</sub> for a given starting product (1). (b) The photolysis of (1) in PhCl also leads principally to loss of neopentane with the apparent formation of (4).<sup>§</sup> This species is *inactive* as a catalyst, but on addition of AlBr<sub>3</sub>, *cis*-pent-2-ene is exceedingly rapidly metathesised (initial rate >5000 mol min<sup>-1</sup>) and i.r. spectra show cleavage of the oxo-bridges to occur by co-ordination to aluminium.

TABLE. Selected spectroscopic data.

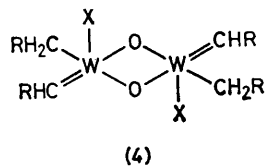
Compound	<sup>1</sup> H N.m.r. <sup>a</sup> δ(W-CH <sub>2</sub> )	ν(W=O) <sup>c</sup>	I.r. <sup>b</sup> ν(W-X)	ν(OAY <sub>n</sub> )
W(O)ClR <sub>3</sub>	2.59	978	284	—
W(OAlCl <sub>3</sub> )ClR <sub>3</sub>	3.53	952	308	536, 454, 362, 347
W(O)BrR <sub>3</sub>	2.62	979	<200	—
W(OAlBr <sub>3</sub> )BrR <sub>3</sub>	3.54	939	<200	441, 416, 338
W(OBBr <sub>3</sub> )BrR <sub>3</sub>	3.66	978	<200	1014, 999, 667, 658, 642
W(O)(OR)R <sub>3</sub>	1.95	945	648	—
W(OAlBr <sub>3</sub> )(OR)R <sub>3</sub>	2.85	925	680	429
W(OSnCl <sub>4</sub> )(OR)R <sub>3</sub>	2.68	860	670	372, 345, 318
W(OMgBr <sub>2</sub> )(OR)R <sub>3</sub>	2.57	898	661	349
W(OZnCl <sub>2</sub> )(OR)R <sub>3</sub>	2.52	915	669	345, 318, 244

<sup>a</sup> In C<sub>6</sub>D<sub>6</sub>, δ(W-CH<sub>2</sub>-CMe<sub>3</sub>); Me<sub>4</sub>Si internal reference. <sup>b</sup> In cm<sup>-1</sup> (Nujol mull). <sup>c</sup> This vibration is coupled with ν(OAY<sub>n</sub>) vibrations on complexation.

<sup>†</sup> This large variation results from mixing of ν(W=O) with ν(OAY<sub>n</sub>) modes.

<sup>‡</sup> X-Ray structural studies confirm this conclusion (J. Fischer and L. Ricard, to be published).

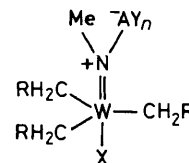
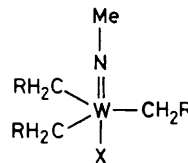
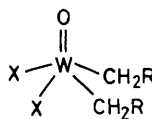
<sup>§</sup> Complex (4) can be observed spectroscopically (i.r. and <sup>1</sup>H n.m.r.) but has proved difficult to obtain free from impurities in the solid state.



Two other related families of complexes show like behaviour.  $WO(OR)_2(CH_2R)_2$  (5) is prepared by treating  $WOCl_2(OR)_2$  with  $(RCH_2)_2Mg$  in ether. Adduct formation is again observed with  $AlBr_3$ , *via* an oxo-bridge, but subsequent loss of neopentane and catalytic activity occur *in the absence of light*.

Other ligands can serve a bridging role; hence the iso-electronic imido-group in (6), prepared by alkylation of  $W(NMe)Cl_4$ , also binds Lewis acids to form (7). Interestingly, for  $X=Br$ , photoinitiation is necessary for catalytic activity; for  $X=Cl$ , the catalyst functions in absence of light.

The Lewis acid thus plays a role in both initiation and propagation in these catalysts. The co-ordination of the Lewis acid *via* a ligand bridge such as an oxo-bridge<sup>3</sup>



creates greater electron deficiency at the transition metal centre.<sup>4</sup> This facilitates (a) reductive  $\alpha$ -elimination processes of ( $W^{VI} \rightarrow W^{IV}$ ) causing neopentane loss and carbene formation;<sup>5</sup> and (b) easier electrophilic attack of the carbene complex on the reactant olefin. Further, co-ordination of the Lewis acid to the most electron-rich ligand impedes dimerisation *via* this ligand which would otherwise block a vacant site and hence prevent olefin co-ordination.

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<sup>1</sup> J. Kress, M. J. M. Russell, M. G. Wesolek, and J. A. Osborn, *J. Chem. Soc., Chem. Commun.*, 1980, 431. Note  $MOR_4$  must be reformulated  $MO(OR)_3$  (to be published).

<sup>2</sup> See also J. H. Wengrovius, R. R. Schrock, M. R. Churchill, J. R. Missert, and W. J. Youngs, *J. Am. Chem. Soc.*, 1980, **102**, 4515; E. L. Muetterties and E. Band, *ibid.*, p. 6572; J. McGinnis, T. J. Katz, and S. Hurvitz, *ibid.*, 1976, **98**, 605.

<sup>3</sup> For an alternative view see: A. K. Rappé and W. A. Goddard, III, *J. Am. Chem. Soc.*, 1980, **102**, 5114.

<sup>4</sup> See also: F. N. Tebbe, G. W. Parshall, and G. S. Reddy, *J. Am. Chem. Soc.*, 1978, **100**, 3611.

<sup>5</sup> Cf. C. D. Wood, S. J. McLain, and R. R. Schrock, *J. Am. Chem. Soc.*, 1979, **101**, 3210.