

# ALKOXY CHEMISTRY OF TRANSITION METALS—LINKS WITH COORDINATION AND ORGANOMETALLIC CHEMISTRY

R C MEHROTRA FNA AND A SINGH

*Chemical Laboratories, University of Rajasthan, Jaipur 302004, India*

*(Received 15 February 1988; Accepted 13 October 1988)*

In this review a brief account of the synergetic developments in the theories of coordination chemistry and elucidation of structural features of simple and polymetallic alkoxides has been presented. This is followed by an overview of the enhancing role of metal alkoxides and aryloxides in organotransition metal chemistry.

**Key Words :** Transition Metal Alkoxides; Coordination and Organometallic Chemistry

## COORDINATION MODEL FOR SIMPLE AS WELL AS POLYMETALLIC ALKOXIDES

### *Introduction*

Beginning with only a few metals and metalloids (e.g., Si, B, Al, Mg, Na, K, Ti) in 1950, the alkoxy chemistry of almost all the elements in the periodic table has been elucidated.<sup>1-5</sup> A renaissance in Inorganic Chemistry occurred almost simultaneously in early fifties with a more refined development of crystal and ligand field theories and their applications to spectroscopic and magnetic properties of coordination compounds of transition metals.<sup>6</sup> Although a few organometallic derivatives of transition metals had been discovered, rapid developments in this field also began with the synthesis of  $C_6H_5Ti(OPr^t)_3$  by Herman and Nelson<sup>7</sup> in 1952 and  $Fe(C_5H_5)_2$  by Pauson<sup>8</sup> in 1951.

In this review, an account would be presented of the rationalisation of alkoxy chemistry of transition metals on a simple coordination model followed by a brief account of organometallic chemistry of transition metals supported by alkoxide ligands.

## STRUCTURAL FEATURES OF TRANSITION METAL ALKOXIDES

The structural features of simple monometallic as well as bi- and higher polymetallic alkoxides can be easily explained on the basis of formation of associated<sup>9</sup> species endowing on the metals the desired coordination state. The main parameters determining the choice of a particular structural type are: (i) the empirical formula  $M(OR)_n$  of a homopolar and  $X_xM(OR)_{n-x}$  of a heteropolar species; (ii) the size and the formal oxidation state of the metal atom; (iii) The bulk (ramification) of the alkyl group; and (iv) the  $d^n$  configuration of the transition

metal. Although only a few actual X-ray structures are available, yet the information from these coupled with a large amount of data from spectroscopic and other physico-chemical measurements indicates the information of the following general prototypes<sup>5,2h</sup>:

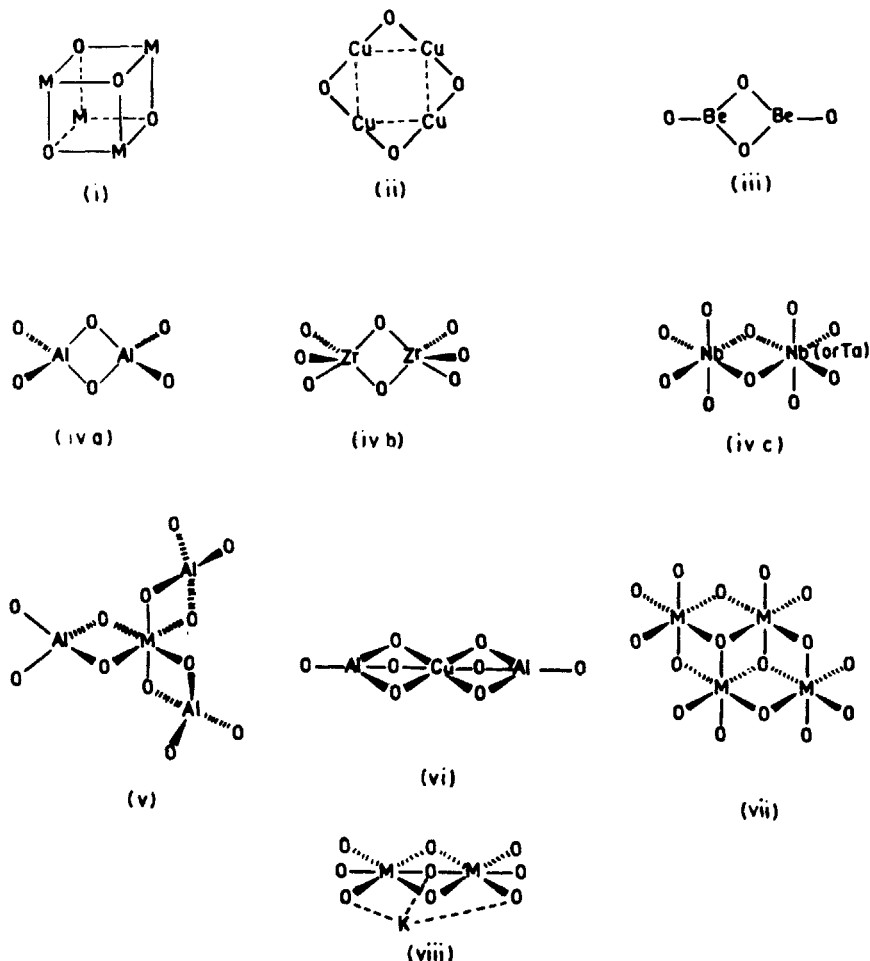


FIG 1 Prototypical structures for small oligomeric metal alkoxides :

- (i) the cubane  $M_4O_4$  unit in  $\{Ti(OR)_4\}$  and  $\{Na(OBu^t)_4\}$ ;
- (ii) the planar  $\{Cu(OBu^t)_4\}$ ;
- (iii) trigonal units in  $\{Be(OR)_2\}_2$ ;
- (iv) edge shared (a) tetra-, (b) penta-, and (c) octahedral units in  $\{Al(OBu^t)_3\}_2$ ,  $(Bu^tO)_2 Zr(\mu-Ome)_2 Zr(OBu^t)_2$ , &  $\{Nb(OMe)_5\}_2$  or  $(MeO)_4 Nb(\mu-Ome)_2 Ta(OMe)_4$  respectively;
- (v) tetra- and octahedral units in  $M\{Al(OPr')_4\}_2$  with  $M = Al, Cr$  or  $Ln$ ;
- (vi)  $(Pr'O) Al(\mu-OPr')_3 Cu(\mu-OPr')_3 Al(OPr')$ ;
- (vii) octahedral units in  $\{M(OEt)_4\}_4$  with  $M = Ti, V, W$ ; and
- (viii) octahedral units in  $KU_2(OBu^t)_6$  (Cotton and coworkers,<sup>10b</sup> 1984) and  $KZr_2(OPr')_6$  (A Mehrotra<sup>3</sup> 1972)

The effect of bulkier ligands in lowering the degree of association can be illustrated by freshly distilled trimeric  $\{\text{Al}(\text{OPr}^t)_3\}_3$  getting aged<sup>2a</sup> to tetrameric  $\{\text{Al}(\text{OPr}^t)_3\}_4$ , which has been shown by Turova *et al.*,<sup>10a</sup> to have structure 'v' (Fig. 1) with central octahedral aluminium atom surrounded by three four-coordinate aluminium atoms. By contrast,  $\{\text{Al}(\text{OBu}^t)_3\}_2$  has a dimeric tetrahedral structure (iv) (in Fig. 1).

Bivalent metals {like alkaline earths, Cr(II), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II)} generally tend to form polymeric structures with the central metal in 6- or 4-coordinated forms depending upon the bulk of the alkyl group. Most of these are non-volatile and insoluble in organic solvents. However, with bulkier alkoxy ligands, a number of monomeric derivatives of later '3d' metals have also been described, e.g.,  $\text{Co}(\text{OCHBu}_2)_2$ ,<sup>11</sup>  $\text{Cr}(\text{OCBu}^t)_2$ ,  $\text{LiCl}(\text{THF})_2$ ,<sup>12</sup>  $\text{CoCl}(\text{OCBu}^t)_2$ ,  $\text{Li}(\text{THF})_3$ ,<sup>13</sup> and  $\text{Co}\{\text{OCPh}_3\}_2$   $(\text{THF})_2$ .<sup>14</sup>

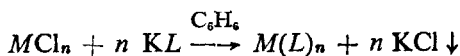
Even the polymeric non-volatile alkoxy derivatives of bivalent metals could be converted into volatile, soluble, monomeric, bimetallic alkoxides<sup>2a,2d</sup> with  $\{\text{Al}(\text{OPr}^t)_4\}^-$  ligand, which is generally bidentate, but in some cases like copper, it appears to become tridentate with the structure-vi (Fig. 1) mainly due to a strong tendency of copper (II) to assume octahedral form<sup>15</sup>.

The studies on bimetallic alkoxides of later transition metals have now been extended with similar results to the ligands like<sup>16a,b</sup>  $\{\text{Nb}(\text{OPr}^t)_6\}^-$  and  $\{\text{Ta}(\text{OPr}^t)_6\}^-$  as well as<sup>17-19</sup>  $\{\text{Zr}_2(\text{OPr}^t)_9\}^-$ . More recently, volatile monomeric and soluble tri- and tetra-metallic alkoxides of later transition metals<sup>20</sup> have been synthesised by more than one type of ligands bound to the same central metal atom. The varieties of bi- and higher poly-metallic alkoxides synthesised during the last few years can be illustrated by the following examples, with a few typical ligands represented by symbols given in parentheses,  $\{\text{Al}(\text{OPr}^t)_4\}^-$  ( $L_{A1}$ );  $\{\text{Zr}_2(\text{OPr}^t)_9\}^-$  ( $L_{Zr}$ ) and  $\{\text{Nb}(\text{OPr}^t)_6\}^-$  or  $\{\text{Ta}(\text{OPr}^t)_6\}^-$  ( $L_{\text{Nb/Ta}}$ ):-

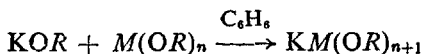
- (i)  $M(L_{A1})_n$  where  $M = \text{Li, Na, K, Rb, Cs, Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg, Ga, In, Sc, Y, Ln, Th, Sn(IV), Cr(III), Mn(II), Fe(II \& III), Co(II), Ni(II), Cu(II)}$  and 'n' is the valency of the central metal  $M$ .
- (ii)  $(\text{Pr}^t\text{O})_2 \text{Zr}(L_{A1})_2$ ;  $(\text{Pr}^t\text{O})_3 \text{Nb}(L_{A1})_2$ .
- (iii)  $M(L_{Zr})_n$  and  $M(L_{\text{Nb/Ta}})_n$  where  $M = \text{An alkali or alkaline earth metal, Cr(III), Fe(II and III), Ni(II) and Cu(II)}$ .
- (iv)  $\{\text{Pr}^t\text{O}\} \text{Be}L_{A1} \}_2$ ;  $L_{Zr}\text{Be}L_{A1}$
- (v)  $\{\text{ClML}_{A1}\}$ ,  $M = \text{Co(II), Ni(II), Cu(II)}$ ;  
 $\{\text{ClML}_{Zr}\}$ ,            "            "            "
- (vi)  $\text{ClFe}(L_{A1})_2$ ;  $\text{Cl}_2\text{Fe}(L_{A1})$ ;  $\text{ClFe}(L_{Zr})_2$ ,  $\text{Cl}_2\text{Fe}(L_{Zr})$ ; and the derivatives of groups V and VI in which chlorine(Cl) has been substituted by an alkoxy group (OR).
- (vii)  $L_{A1}ML_{\text{Nb}}$ ;  $Z_{A1}ML_{\text{Ta}}$ ;  $L_{A1}ML_{Zr}$ ,  $L_{\text{Ta}}ML_{Zr}$ , etc., where  $M = A$  bivalent later '3d' transition metal.

(viii)  $FeL_{Al}L_{Zr}L_{Ta}$ 

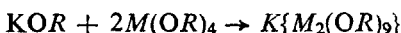
These novel bi- and poly-metallic alkoxides can be synthesised in quantitative yields by simple reactions represented by the following equations :



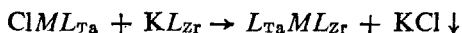
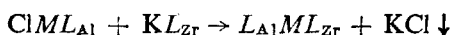
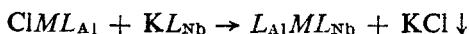
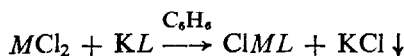
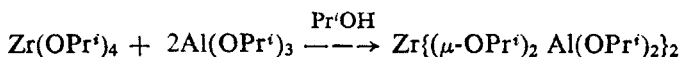
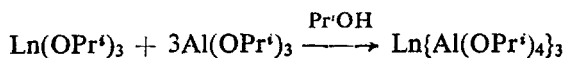
(where  $L$  represents  $L_{Al}$ ,  $L_{Zr}$  or  $L_{Nb/Ta}$ )



(where  $M = Al, Ga, Nb, Ta, Fe(III), \text{etc.}$ )



(where  $M = Ti, Zr, Hf, Th, U(IV)$ )



In the case of trivalent metals like Fe(III), the above types of reactions can be carried out in three stages resulting in monomeric products like  $M(L_{Al})$  ( $L_{Zr}$ ) ( $L_{Ta}$ ).

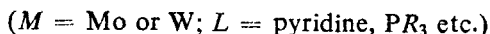
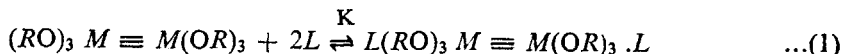
All the above bi- and poly-metallic alkoxides are monomeric and can be volatilised (except for niobium and tantalum derivatives) under reduced pressure. The spectroscopic and magnetic properties of all the bi- and polymetallic alkoxides can be explained on the basis of the ligands ( $L$ ) behaving as bi- and (under certain circumstances) as tridentate coordinating ligands.

## ORGANOMETALLIC CHEMISTRY SUPPORTED BY ALKOXIDE (ARYLOXIDE) LIGANDS

*Introduction*

The development of organometallic chemistry of transition metals has often centred around a proper choice of soft,  $\pi$ -acceptor ancillary ligands such as carbon monoxide, tertiary phosphines, cyclopentadienyls and cyclooctadiene. Alkoxide ligands,  $RO^-$ , share some features with the above. For example,  $RO^-$  ligands also (like CO) may occupy either terminal or bridging positions and their facile interchange endows fluxional behaviour in polynuclear compounds. Bulky  $RO^-$  ligands favour specific coordination states for the central metal atom in a manner similar to bulky phosphines or substituted cyclopentadienyls.

Alkoxide ligands are electronically flexible. The degree of  $\pi$ -donation can respond to the needs of a metal atom, which may change with the substrate uptake or release. The position of equilibrium in equation (1) is determined<sup>21</sup> by the metal Mo or W, the bulkiness of R and L, the nature of L, and the temperature :

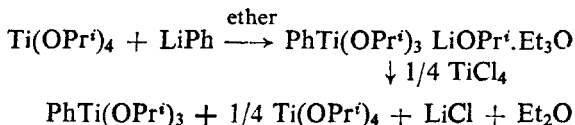


The formal electron count at each metal does not change with Lewis base association or dissociation. In forming a  $M-L$   $\sigma$  bond, one  $M-OR$   $\pi$  bond is sacrificed and on breaking a  $M-L$   $\sigma$  bond, one  $M-OR$   $\pi$  bond is formed. The degree of  $\pi$ -donation of an OR ligand is generally delocalized, but some factors (e.g., *trans* influence, and neighbouring ligands) may oppose this and cause  $M-OR$  bond to localize. In general, the electron releasing strength of OR ligands (both  $\sigma$  and  $\pi$ ) follows the order : *t*-BuO > *i*-Pro > *t*-BuCH<sub>2</sub>O > EtO.

Besides other similarities, a number of isolobal relationships are becoming apparent. The  $d^2-M(OR)_4$  and  $d^3-M(OR)_3$  units (where  $M = \text{Mo or W}$ ) are isolobal with say Fe(CO)<sub>4</sub> (16 electron system) and Co(CO)<sub>3</sub> (15 electron fragment) respectively.

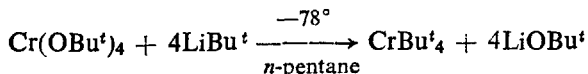
#### Alkylation (Arylation, Benzoylation) Reactions

The first Ti-C  $\sigma$  bonded compound C<sub>6</sub>H<sub>5</sub>Ti(OPr<sup>t</sup>)<sub>3</sub> was described in 1952 by Herman and Nelson:<sup>8</sup>

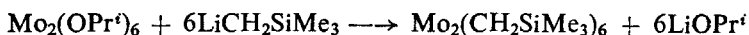


It may be of interest to note that a fairly volatile (stable) product MeTi(OPr<sup>t</sup>)<sub>3</sub> has been later synthesised by Rausch and Gordon<sup>22</sup> by the reaction between ClTi(OPr<sup>t</sup>)<sub>3</sub> and LiMe in ether at -10 °C. With a bulkier alkoxy ligand, stable dimethyl derivatives, Me<sub>2</sub>M(OCBu<sup>t</sup>)<sub>2</sub> (where  $M = \text{Ti or Zr}$ ) have been described recently by Wolczanski *et al.*<sup>23</sup>

This simple route has not been exploited much except in a few cases; for example, the reaction of Cr(OBu<sup>t</sup>)<sub>4</sub> with LiBu<sup>t</sup> has been found by Wilkinson<sup>24</sup> *et al.* to give much higher yields of CrBu<sup>t</sup><sub>4</sub> than the reaction of CrCl<sub>3</sub>·3 THF:

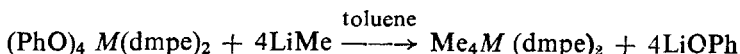


Similarly, alkylation of (MoCl<sub>3</sub>)<sub>n</sub> with LiCH<sub>2</sub>SiMe<sub>3</sub> yields the dinuclear complex Mo<sub>2</sub>(CH<sub>2</sub>SiMe<sub>3</sub>)<sub>6</sub> in less than 25 per cent yield, whereas the yield from Mo<sub>2</sub>(OPr<sup>t</sup>)<sub>6</sub> is about 75 per cent:<sup>25</sup>

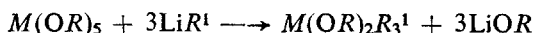


Seebach and coworkers<sup>26</sup> have developed an interesting chemistry of mixed alkyl alkoxides of titanium and zirconium and their applications in organic syntheses.

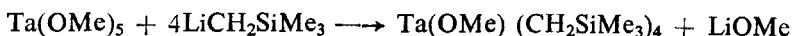
Similarly,  $\text{Me}_4\text{M}(\text{dmpe})_2$  derivatives of thorium and uranium have been synthesized from their phenoxides<sup>27</sup>:



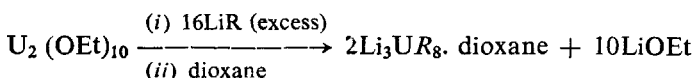
In contrast to chromium, molybdenum and thorium, the alkylation of alkoxides of niobium and tantalum generally leads to partially substituted products:<sup>25</sup>



(where  $R = \text{Me}, \text{Pr}^t, \text{C}_6\text{H}_3\text{Me}_2-2, 6$  and  $R^1 = \text{Me}, \text{CH}_2\text{CMe}_3$ )



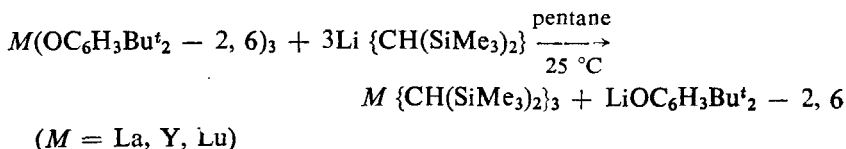
The reaction of  $\text{U}(\text{OEt})_5$  with  $\text{LiR}$  ( $R = \text{Me}, \text{CH}_2\text{CMe}_3, \text{CH}_2\text{SiMe}_3$ ) followed by dioxane precipitation yields lithium octaalkyluranate (V):<sup>28</sup>



The synthesis of 'ate' complexes of lanthanons has also been reported by Schumann<sup>29</sup> by simple metathetic reaction of  $\text{M}(\text{OBu}^t)_3$  ( $M = \text{Er}, \text{Lu}$ ) with four equivalents of  $\text{LiBu}^t$  in TMEDA:

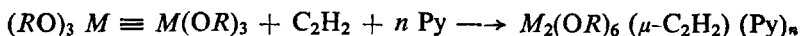


Furthermore, with the use of recently synthesized three coordinate lanthanon aryloxides,<sup>30,31</sup> a novel and facile route for synthesis of lanthanon alkyls has been achieved by Lappert and coworkers<sup>32</sup> as illustrated below:



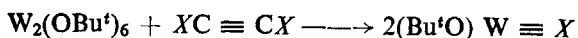
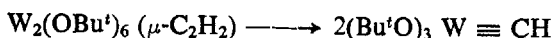
#### *Alkyne, Alkylidyne and Alkylidene Derivatives*

The reactions between  $\text{M}_2(\text{OR})_6$  ( $M \equiv M$ ) with alkynes have been extensively employed for the synthesis of metal *alkyne* complexes<sup>33,34</sup>:

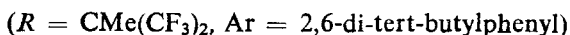
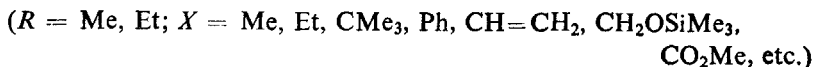


(where  $M = \text{Mo}$  or  $\text{W}$  and  $n = 1$  or  $2$ ).

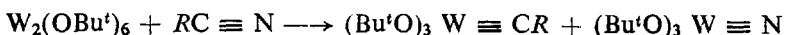
In addition, a considerable amount of novel metal *alkylidyne* chemistry has been recently developed by the metathesis reactions<sup>35-37</sup> of  $\text{M} \equiv \text{M}$  and  $\text{C} \equiv \text{C}$  bonds:



or

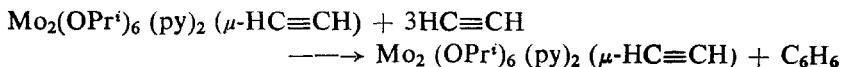
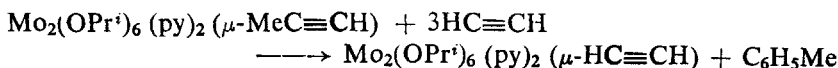


Within this context, the remarkable metathetic reactions involving  $W_2(OBu^t)_6$  and  $RC \equiv N$  ( $R = \text{alkyl or aryl}$ ) may be viewed as oxidative cleavage which are favourable for  $W^{35a}$  but not for Mo compounds:

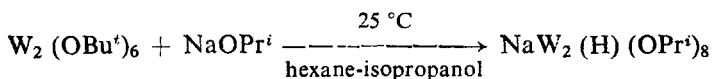


The  $M_2(OR)_6$  compounds also react with other  $\pi$ -acceptor ligands such as CO to form 1:1 adducts of the type  $M_2(OBu^t)_6 (\mu-CO)$  and  $M_2(OR)_6 (\mu-CO)(py)_2$  (where  $M = Mo$  or  $W$ ;  $R = Pr^t$  or  $CH_2CMe_3$ ) which may be viewed in terms of redox reactions between the  $\pi$ -acceptor ligand and the  $M \equiv M$  bond as the donor<sup>33,34</sup>.

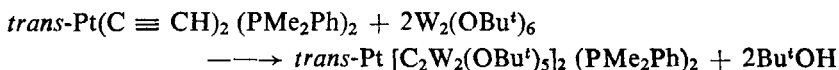
Catalytic cyclization of alkynes<sup>33</sup> ( $C_2H_2$  and  $C_2Me_2$ ) by  $Mo_2(OR)_6$  compounds has also been observed:



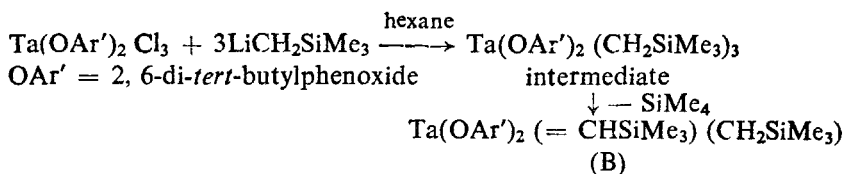
The reactions involving either  $W_2(OBu^t)_6$  or  $W_2(OPr^t)_6 (HNMe_2)_2$  in hexane-isopropanol solvent with  $NaOPr^t$  yield  $NaW_2(H)(OR)_8$  which can be isolated in crystalline form as a diglyme adduct:<sup>37</sup>



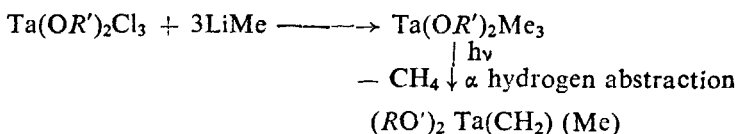
The side product obtained (in *ca.* 5-10 per cent yields) during the preparation of  $W_2(OPr^t)_6 (HNMe_2)_2$  has been characterized as the carbido cluster<sup>33,38</sup>  $W_4(\mu_4-C)(\mu-NMe)(OPr^t)_{12}$ :



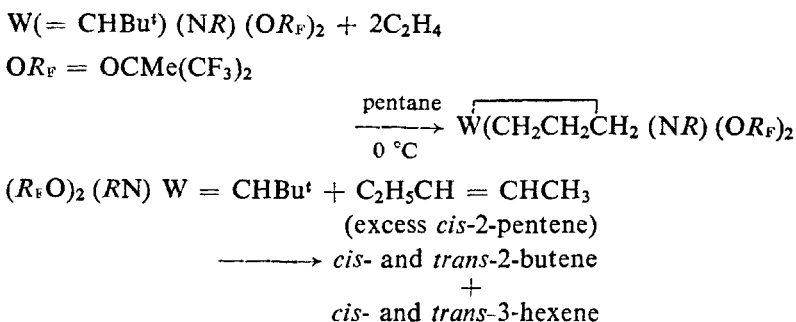
Alkoxide ligands sometimes appear to play an important side-role in the preparation of metal alkylidene complexes<sup>39</sup> as depicted :



The product (B) is probably formed<sup>25,40a,b</sup> by  $\alpha$ -hydrogen atom abstraction process (which is less frequent than the well-known  $\beta$ -hydrogen elimination):

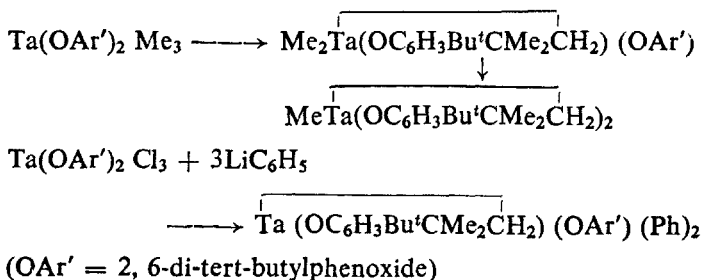


These alkoxy (or aryloxy) supported alkylidene complexes are highly active, olefin metathesis catalysts. These catalytic reactions are believed to proceed via the formation and decomposition of metallacycles.<sup>41-43</sup> Few typical examples are illustrated below:



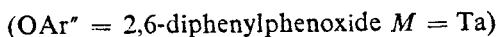
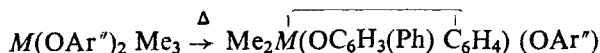
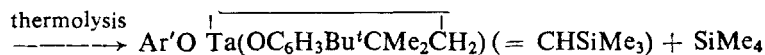
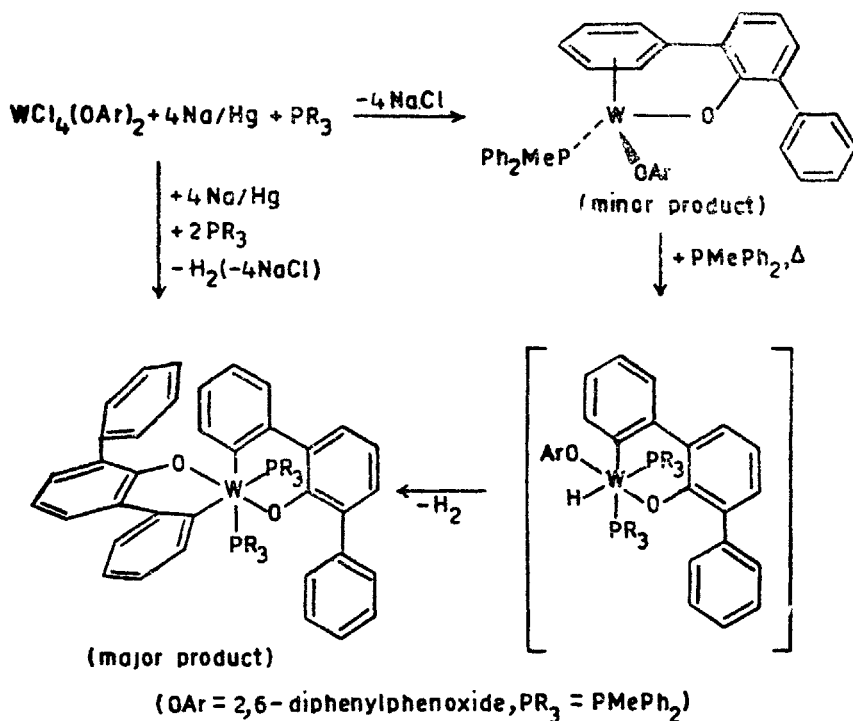
### Cyclometallation Reactions

As indicated earlier, there is currently considerable research interest in the organometallic chemistry associated with sterically demanding aryloxy ligation. In most cases bulky 2,6-di-*tert*-butylphenoxide group is present as an ancillary (or supporting) ligand. However, the ligand itself has been found, under sometimes mild conditions, to undergo cyclometallation reactions to form six-membered metallacycle rings derived by activation of one of the carbon-hydrogen bonds of a *tert*-butyl group or a phenyl group attached to phenoxide ring<sup>44,45</sup>:



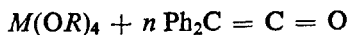


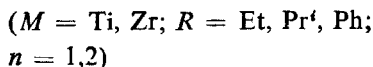
Recently, the ligation of the 2,6-diphenylphenoxide ligand to group VI metal centres resulted in bonding modes in which the ligand could be chelated to the metal either *via* an  $\eta^6$ -interaction or else through a metal-carbon  $\sigma$ -bond to the arene side groups<sup>46</sup> :



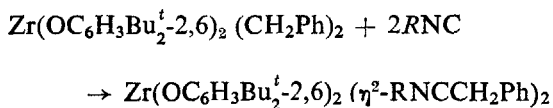
#### *Insertion of Unsaturated Organic Substrates into Metal-Alkoxide and Metal-Alkyl Bond*

As metal alkoxides are in general a highly reactive group of complexes, ketenes are found to readily insert into Ti-OR or Zr-OR bonds to generate new organometallics<sup>47</sup>:

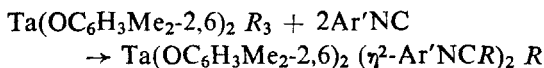




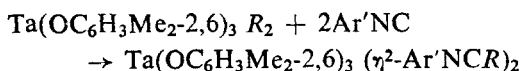
Furthermore, the reaction of arylisocyanides with mixed alkyl-aryloxides of zirconium and tantalum allows the isolation of the corresponding new iminoacyl derivatives.<sup>48,49</sup>



( $R = \text{Bu}^t$ , 2,6-dimethylphenyl)



( $R = \text{Me, CH}_2\text{C}_6\text{H}_5$ ;  $\text{Ar}' = 2,6$ -dialkylphenyl)



( $R = \text{CH}_2\text{C}_6\text{H}_5$ ;  $\text{Ar}' = 2,6$ -dimethylphenyl)

#### REFERENCES

- 1 D C Bradley, R C Mehrotra and D P Gaur *Metal Alkoxides* Academic Press London (1978)
- 2 (a) R C Mehrotra *J Indian chem Soc* **30** (1953) 385  
(b) R C Mehrotra *Inorg Chim Acta Rev* **1** (1957) 99  
(c) R C Mehrotra *Coord Chem (IUPAC)* **21** (1981) 113  
(d) R C Mehrotra *J Indian chem Soc* **59** (1982) 715  
(e) R C Mehrotra *Proc Indian natn Sci Acad* **54A** (1986) 954  
(f) R C Mehrotra *J non-cryst Solid* **100** (1988) 1  
(g) R C Mehrotra Platinum Jubilee Lecture Publ Indian Sci Congr (1988)  
(h) R C Mehrotra *Mater Res Soc Publ* (1988)  
(i) R C Mehrotra, P N Kapoor and J M Batwara *Coord Chem Rev* **31** (1980) 67
- 3 A Mehrotra *PhD Thesis* Univ Rajasthan (1972)
- 4 R C Mehrotra, Y P Singh and S K Agarwal *Coord Chem Rev* **68** (1985) 100
- 5 M H Chisholm and I P Rothwell In: *Comprehensive Coordination Chemistry* (Eds G Wilkinson, R D Gillard and J A McCleverty) Pergamon Press UK (1987) Vol 2 Chap 15.3 pp 335-364
- 6 *Comprehensive Coordination Chemistry* (Eds G Wilkinson, R D Gillard and J A McCleverty) Pergamon Press UK (1987) Vols 1,3,4
- 7 D F Herman and W K Nelson *J Am chem Soc* **74** (1952) 2693
- 8 T J Kealy and P L Pauson *Nature* **168**(1951) 1039
- 9 D C Bradley *Nature* **182** (1958) 1211
- 10 (a) N Ya Turova, V A Kozunov, A I Yanovskii, N G Bokii, Bu T Struchkov and B L Tarnopol'sku *J inorg nucl Chem* **41** (1979) 5  
(b) F A Cotton, D O Marler and W Schwotzer *Inorg Chem* **23** (1984) 4211
- 11 M Bochmann, G Wilkinson, G B Young, M B Hursthouse and K M A Malik *J chem Soc Dalton Trans* (1980) 1863
- 12 H Hvosllef, H Hope, B D Murray and P P Power *J chem Soc chem Commun* (1983) 1438

- 13 M M Olmstead, P P Power and G Sigel *Inorg Chem* **25** (1986) 1027
- 14 G A Sigel, R A Bartlett, D Decker, M M Olmstead and P P Power *Inorg Chem* **26** (1987) 1773
- 15 R C Mehrotra and J Singh *Z anorg allg Chem* **522**(1984) 211
- 16(a) R K Dubey, A Singh and R C Mehrotra *Bull chem Soc Japan* **61** (1988) 683  
(b) R K Dubey, A Singh and R C Mehrotra *J organometal Chem* **341** (1988) 569
- 17 S K Agarwal and R C Mehrotra *Inorg Chim Acta* **112** (1986) 117
- 18 R K Dubey, A Singh and R C Mehrotra *Polyhedron* **6** (1987) 427
- 19 R K Dubey, A Singh and R C Mehrotra *Inorg Chim Acta* **118** (1986) 151
- 20 R K Dubey, A Shah, A Singh and R C Mehrotra *Recl Trav Chim Pays Bas* **107** (1988) 237
- 21(a) M H Chisholm, F A Cotton, M W Extine and W W Reichert *J Am chem Soc* **100** (1978) 153  
(b) M H Chisholm *Polyhedron* **2** (1983) 681 and references therein
- 22 M D Rausch and H B Gordon *J organometal Chem* **74** (1974) 85
- 23 T V Lubben, P T Wolczanski and G D van Duyn *Organometallics* **3** (1984) 977
- 24 W Mowat, A J Shortland, N J Hill and G Wilkinson *J chem Soc Dalton Trans* (1973) 770
- 25 L Chamberlain, J Keddington and I P Rothwell *Organometallics* **1** (1982) 1098
- 26(a) D Seabach *et al.* *Modern Synthetic Methods* (Ed R Sheffield) Wiley New York (1983)  
(b) D Seabach, A K Beck, M Schiess, L Wilder and A Wonnacott *Pure Appl Chem* **55** (1983) 1807
- 26 (c) D Seabach and V Prelog *Angew Chem Int Ed Engl* **21** (1982) 654
- 27 P G Edwards, R A Anderson and A Zalkin *J Am chem Soc* **103** (1981) 7792
- 28 E R Sigurdson and G Wilkinson *J chem Soc Dalton Trans* (1977) 812
- 29 H Schumann In: *Organometallics of the f-Elements* (Eds T J Marks and R D Fischer) Reidel Dordrecht (1979) 103
- 30 P B Hitchcock, M F Lappert and A Singh *J chem Soc chem commun* (1983) 1499
- 31 M F Lappert, A Singh and R G Smith *Inorg Synth* (1988)
- 32 M F Lappert and R G Smith (*to be published*)
- 33 M H Chisholm, K Folting, J C Huffman and I P Rothwell *J Am chem Soc* **104** (1982) 4389
- 34 M H Chisholm and W E Buhro *Adv organometal Chem* (1988)
- 35(a) R R Schrock, M L Listemann and L G Sturgeoff *J Am chem Soc* **104** (1982) 4291  
(b) R R Schrock, I A Weinstock, A D Horton, A H Liu and M H Schofield *J Am chem Soc* **110** (1988) 2686
- 36 M H Chisholm, D M Hoffman and J C Huffman *Chem Soc Rev* **14** (1985) 69
- 37 M L Listemann and R R Schrock *Organometallics* **4** (1985) 74 and references therein
- 38(a) M H Chisholm, K Folting, J C Huffman, J Leonelli, N S Marchant, C A Smith and L C E Taylor *J Am chem Soc* **107** (1985) 3722
- 38(b) R J Blau, M H Chisholm, K Folting and R J Wang *J chem Soc chem Commun* (1985) 1582
- 39 R R Schrock *ACS Symp Ser* **221** (1983) 369
- 40(a) L R Chamberlain, A P Rothwell and I P Rothwell *J Am chem Soc* **106** (1984) 1847  
(b) L R Chamberlain and I P Rothwell *J chem Soc Dalton Trans* (1987) 155
- 41 C J Schaverien, J C Dewan and R R Schrock *J Am chem Soc* **108** (1986) 2771
- 42 R R Schrock, R T De Pue, J Feldman, C J Schaverien, J C Dewan and A H Liu *J Am chem Soc* **110** (1988) 1423
- 43 J P Collman, L S Hegedus, J R Norton and R G Finke *Principles and Applications of Organotransition Metal Chemistry* Univ Sci California (1987)
- 44 I P Rothwell *Polyhedron* **4** (1985) 117 and references therein
- 45 I P Rothwell *Accs chem Res* **21** (1988) 153 and references therein
- 46 J L Kerschner, I P Rothwell, J C Huffman and W E Streib *Organometallics* **7** (1988) 1871 and references therein
- 47 C Blandy and D Gervais *Inorg Chim Acta* **47** (1981) 197
- 48 A K Mc Mullen and I P Rothwell *J Am chem Soc* **107** (1985) 1072
- 49 L R Chamberlain, I P Rothwell and J C Huffman *J chem Soc chem Commun* (1986) 1203