

## Bis-organoimido Complexes of Tungsten(vi). The Crystal and Molecular Structure of Bipyridyldichlorobis(phenylimido)tungsten(vi), $[\text{WCl}_2(\text{NPh})_2(\text{bipy})]$

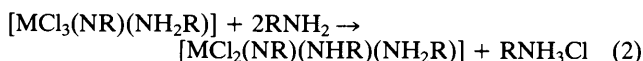
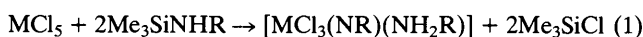
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Bis-organoimido complexes of tungsten(vi) are prepared by reaction of  $\text{WCl}_6$  with  $\text{Me}_3\text{SiNHCMe}_3$ , or by reaction of mono-organoimido complexes with the silylamines  $\text{Me}_3\text{SiNHR}$ ; the structure of  $[\text{WCl}_2(\text{NPh})_2(\text{bipy})]$  ( $\text{bipy} = \alpha, \alpha\text{-bipyridyl}$ ) has been established by X-ray crystallography.

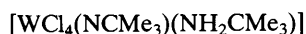
Preparative routes leading to bis-organoimido complexes,  $[\text{M}(\text{NR})_2]$ , are less well developed than those for mono-organoimido complexes.<sup>1</sup> We have previously shown<sup>2</sup> that for  $\text{MCl}_5$  molecules, ( $\text{M} = \text{Nb}, \text{Ta}$ ), substitution of two chlorides by alkylamido ligands,  $\text{NHR}$ , results in formation of an alkylimido ligand and co-ordinated primary amine [equation (1)] by an interligand proton-transfer process which is independent of steric size. A third alkylamido ligand could be substituted [equation (2)] but the complex could not be induced to eliminate  $\text{HCl}$  to form a second imido function. We have now extended these reactions to establish whether two alkylimido ligands can be generated from an  $\text{MCl}_6$  molecule and, if so, whether steric size is important.



Reaction of  $\text{WCl}_6$  with two equivalents of  $\text{Me}_3\text{SiNHCMe}_3$  in benzene gives a yellow product analysing as  $[\text{WCl}_4(\text{NHCMe}_3)_2]$  (1) but  $^{13}\text{C}$  n.m.r. spectroscopy shows it to be a mixture of (1) and  $[\text{WCl}_4(\text{NCMe}_3)(\text{NH}_2\text{CMe}_3)]$  (2). Reaction of the mixture with a further two equivalents of  $\text{Me}_3\text{SiNHCMe}_3$ , or reaction of  $\text{WCl}_6$  with 4 or more equivalents of  $\text{Me}_3\text{SiNHCMe}_3$  gives  $[\text{WCl}_2(\text{NCMe}_3)_2(\text{NH}_2\text{CMe}_3)]_x$  (3) indicated by analytical and  $^{13}\text{C}$  n.m.r. spectral data. A single absorption at  $210\text{ cm}^{-1}$  in the i.r. spectrum indicates *trans* chloro ligands. Complex (3) reacts with  $\gamma$ -picoline (*pic*) or  $\alpha, \alpha\text{-bipyridyl}$  (*bipy*) to form  $[\text{WCl}_2(\text{NCMe}_3)_2(\text{pic})_2]$  (4) and  $[\text{WCl}_2(\text{NCMe}_3)_2(\text{bipy})]$  (5) for which i.r. data indicate *trans* chlorine atoms, while reaction of (3) with  $\text{PMe}_3$  gives  $[\text{WCl}_2(\text{NCMe}_3)_2(\text{PMe}_3)]_x$  (6), for which absorptions at 218 and  $180\text{ cm}^{-1}$  indicate *cis* chlorine atoms. Complex (3) reacts with 4 equivalents of *t*-butylamine in light petroleum (b.p.  $40\text{--}60\text{ }^\circ\text{C}$ ) to give the known complex  $[\text{W}(\text{NCMe}_3)_2(\text{NHCMe}_3)_2]$  (7),<sup>3</sup> which we have as yet been unable to convert into a tris-imido complex.



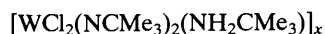
(1)

(5)  $\text{NR} = \text{NCMe}_3$   
(9)  $\text{NR} = \text{NPh}$ 

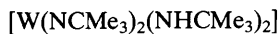
(2)



(6)



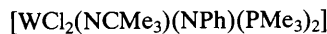
(3)



(7)



(4)



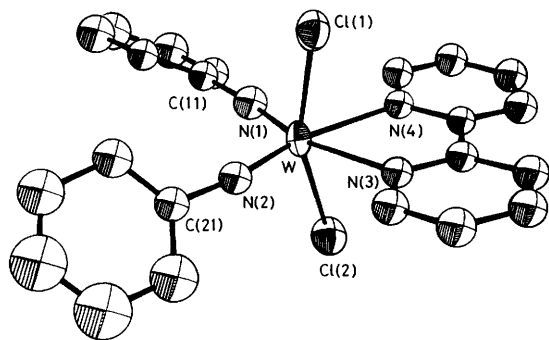
(8)

The silylamines  $\text{Me}_3\text{SiNHR}$  ( $\text{R} = \text{CHMe}_2, \text{Et}$ ) do not react cleanly with  $\text{WCl}_6$  or the mixture of (1) and (2). However, the mono-organoimido tungsten(vi) complexes  $[\text{WCl}_4(\text{NR})_2]$  ( $\text{R} = \text{Ph}, \text{CHMe}_2, \text{Me}$ ), prepared from  $[\text{WCl}_4(\text{O})_2]$  and aryl or alkyl isocyanates,<sup>4</sup> react with the silylamines  $\text{Me}_3\text{SiNHR}'$  ( $\text{R}' = \text{Ph}, \text{PhMe}, \text{CMe}_3, \text{CHMe}_2, \text{CH}_2\text{Me}$ ) in benzene to give the bis-organoimido complexes  $[\text{WCl}_2(\text{NR})(\text{NR}')(\text{NH}_2\text{R}')]_2$ , for which i.r. absorptions in the vicinity of  $310$  and  $270\text{ cm}^{-1}$  indicate *cis*-metal dichloride ligands. Bridging and terminal phenylimido ligands are characterised in the  $^{13}\text{C}$  n.m.r. spectra by *ipso* carbon resonances at  $\delta$  162 and 151 respectively but the  $\alpha$ -carbon resonance position does not distinguish these for the bis alkylimido dimers. However the least sterically hindering organoimido ligand is expected to form the bridge. An X-ray crystal structure determination of  $[\text{WCl}_2(\text{NCMe}_3)(\mu\text{-NPh})(\text{NH}_2\text{CMe}_3)]_2$ <sup>5</sup> has shown bridging *NPh* and terminal *NCMe}\_3* ligands.

The dimers do not react further with primary amines to give complexes similar to (7), but they may be used to form  $[\text{WCl}_2(\text{NR})(\text{NR}')\text{L}_2]$  complexes which cannot be prepared *via* the reaction of the dioxo species  $[\text{WCl}_2(\text{O})_2\text{L}_2]$  with aryl or alkyl isocyanates. Thus reaction of  $[\text{WCl}_2(\text{NCMe}_3)(\mu\text{-NPh})(\text{NH}_2\text{CMe}_3)]_2$  with  $\text{PMe}_3$  gives  $[\text{WCl}_2(\text{NCMe}_3)(\text{NPh})(\text{PMe}_3)_2]$  (8) which contains *trans* orientated phosphines as indicated by a single, virtually coupled triplet for the  $\text{PMe}_3$  ligands in both the  $^{13}\text{C}\{^1\text{H}\}$  and  $^1\text{H}$  n.m.r. spectra and by a singlet (9.6 p.p.m., external  $\text{H}_3\text{PO}_4$ ) in the  $^{31}\text{P}\{^1\text{H}\}$  spectrum. Reaction of the dimers with *bipy* gives the complexes  $[\text{WCl}_2(\text{NR})(\text{NR}')(\text{bipy})]$  for which a single band in the far i.r. spectrum indicates the metal dichlorides are now orientated *trans*. This isomerisation is confirmed by an X-ray crystal structure determination of  $[\text{WCl}_2(\text{NPh})_2(\text{bipy})]$  (9).<sup>†</sup>

The asymmetric unit contains two crystallographically distinct, but structurally similar, molecules. The structure of one of these molecules is depicted in Figure 1 which shows a distorted octahedral geometry about tungsten, with two *cis*-orientated phenylimido groups, *trans* chloro ligands, and the nitrogen atoms of the bipyridyl ring co-ordinated *trans* to the imido functions. The four separate determinations of the imido  $\text{W-N}$  bond lengths and  $\text{W-N-C}$  bond angles are not

<sup>†</sup> Crystal data for (7):  $\text{C}_{22}\text{H}_{18}\text{Cl}_2\text{N}_4\text{W}$ ,  $M = 593.15$ , triclinic, space group  $P\bar{1}$ ,  $a = 14.616(6)$ ,  $b = 17.778(6)$ ,  $c = 8.532(2)$  Å,  $\alpha = 94.71(2)$ ,  $\beta = 100.41(3)$ ,  $\gamma = 84.31(3)^\circ$ ,  $U = 2165.1$  Å<sup>3</sup>,  $F(000) = 1144$ ,  $D_c = 1.819\text{ g cm}^{-3}$ ,  $Z = 4$ ,  $\mu(\text{Mo-K}\alpha) = 64.2\text{ cm}^{-1}$ . Intensity data were recorded on a Nonius CAD4 diffractometer with  $\text{Mo-K}\alpha$  radiation and corrected for Lorentz, polarisation, and absorption effects. The structure was solved from Patterson and heavy-atom electron density syntheses and refined by full-matrix least-squares, omitting hydrogens, with tungsten and chlorine atoms anisotropic, to an  $R$  value of 0.048 for 3357 independent reflections for which  $I > 3\sigma(I)$ . Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.



**Figure 1.** Molecular structure of  $[\text{WCl}_2(\text{NPh})_2(\text{bipy})]$  (**9**). Important averaged bond lengths ( $\text{\AA}$ ) and bond angles ( $^\circ$ ): W–Cl(1) 2.390(4), W–Cl(2), 2.385(4), W–N(1) 1.782(8), W–N(2) 1.775(9), W–N(3) 2.319(8), W–N(4) 2.315(8); W–N(1)–C(11) 165.3(8), W–N(2)–C(21) 166.3(8), N(1)–W–N(2) 104.3(4), Cl(1)–W–Cl(2) 159.3(1).

significantly different [mean values 1.789(6)  $\text{\AA}$  and 165.9(6) $^\circ$  respectively]. Electronically this represents delocalisation of 6 donor electrons over the two phenylimido ligands and thus an 18 electron count for the complex is maintained.

Bis-organoimido complexes of tungsten(VI) may thus be prepared by reactions involving proton transfer from one primary alkylamido group to another. The process is indepen-

dent of steric size, which contrasts with reactions of high-valent early transition metals where, with less acidic  $\alpha$ -hydrogens, metal-alkyl ligands require steric bulk before forming an alkylidene ligand.<sup>6</sup> The new complexes are organoimido analogues of the well-known *cis*-dioxo tungsten(VI) complexes, and the reaction sequences described herein allow their formation for a variety of alkyl and aryl groups.

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