

Preliminary communication

BOND ANGLES AND NON-BONDED DISTANCES IN ALKYL-TRANSITION METAL COMPOUNDS

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(Received January 31st, 1979)

Summary

Application of the steric model of molecular configurations to alkyl-transition metal compounds leads to a rationalisation of the large interbond angles at α carbon atoms, and to intramolecular non-bonded atomic radii for the elements Nb, Ta, Cr, Mo, W, and Pt.

Alkyl-transition metal compounds generally exhibit interbond angles at the α carbon substantially larger than might be expected from the VSEPR* model: since there are usually neither non-bonding electrons nor multiple bonds in the vicinity of C_α , the bond angles at this atom are not easy to rationalise in electronic terms. A simple steric model has been employed [1–3] to rationalise and predict interbond angles MXM' where M, M' are main group elements, and X is a first row element such as carbon, nitrogen, oxygen or fluorine: the basis of this steric model is the hypothesis that in a molecular fragment MXM' , the lower limit of the interbond angle MXM' is determined, for given bonded distances $d(M-X)$ and $d(M'-X)$, by the non-bonded distance $d(M\cdots M')$. This implies that the atoms M and M' are approximately incompressible, so that definite intramolecular radii may be assigned. When the observed angle MXM' is substantially greater than that predicted by the VSEPR model, the limiting value is usually that which is observed, since the electronic contribution strives towards a lowering of the angle: consequently in very many fragments MXM' having large interbond angles, $d(M\cdots M')$ is just the sum of the appropriate intramolecular radii, $r(M) + r(M')$. It is the purpose of this communication to suggest an extension of this model to the transition metals.

If this steric model is applied to alkyl-transition metal compounds, then simultaneously a rationalisation can be made of the interbond angles at C_α , and appropriate intramolecular radii can be derived for the metals. Thus in

*VSEPR = valence shell electron pair repulsion.

(C₅H₅)₂Nb(C₂H₄)C₂H₅, the angle NbCC in the alkyl group is [4] 118.6°, associated with an Nb...C_β distance of 3.319 Å: this implies an upper limit of 2.07 Å for the radius of niobium. Few structures are recorded of simple alkyl compounds, other than methyl compounds, but a number of complexes containing the ligands Me₃CCH₂ and Me₃SiCH₂ have been investigated.

In [(Me₃SiCH₂)₂Cr(bipy)]₂I, the two independent angles CrCC are 127.9 and 128.3°, associated with Cr...Si distances of 3.562 Å and 3.559 Å [5]: the mean *d*(Cr...Si) of 3.56 Å implies a radius of 2.01 Å for chromium, taking the radius of silicon as 1.55 Å [1]. There are two independent molecules in the structure of W₂(CH₂SiMe₃)₆ [6] giving a total of twelve independent W...Si distances: one of the angles WCSi is rather larger than the remainder which are associated with a range of W...Si distances of 3.46–3.51 Å with mean 3.48 Å, so that the radius deduced for tungsten is 1.93 Å. The W...Si distances in the terminal ligands of W₂(CSiMe₃)₂(CH₂SiMe₃)₄ [7] are similar. The molybdenum complex Mo₂(CH₂SiMe₃)₆ has four independent, but similar, molecules in the unit cell [8]: the mean angle MoCSi is 121.1° and the mean distance *d*(Mo—C) is 2.131 Å; however the distance *d*(C—Si) was not reported: using a value of 1.89 Å, the mean observed in the tungsten analogue, a nonbonded distance *d*(Mo...Si) of 3.50 Å is derived implying a molybdenum radius of 1.95 Å. A further example of a Me₃SiCH₂ complex is (Ph₃P)₂Pt(CH₂SiMe₃)Cl in which [9] the Pt...Si distance of 3.33 Å subtends an angle of 116.1° at carbon: the radius implied for platinum is 1.78 Å.

In the tantalum complex Li(dmp)[(Me₃CCH₂)₃TaCCMe₃] (dmp = *N,N'*-dimethylpiperazine) all the angles TaCC exceed the tetrahedral value [10]: although full details of the structure have not been published, all the distances *d*(Ta...C_β) appear to be similar, with a minimum value, found in the unique ligand, of 3.26 Å, suggesting a tantalum radius of 2.01 Å.

There exist a substantial number of Me₃SiCH₂ complexes of other metals which have not been subjected to X-ray analysis; these include (R = Me₃SiCH₂): (C₅H₅)₂MR₂ and MR₄ (M = Ti, Zr, Hf) [11]; VR₄, VOR₃, CrR₄ [12]; ReOR₄ [13]; and Li₂MgR₄ [14]. It seems possible that the structures of these species could be used to derive intramolecular radii for further metals, which radii could in turn be applied to the rationalisation of geometry in other classes of compound. The radii here suggested are collected in Table 1.

One series of alkyl compounds in which the angle MCC is much smaller than expected is M(CH₂Ph)₄ (M = Ti, Zr, Hf), for which it has been suggested that there is a weak bonding interaction between M and the aromatic ring [15–17]. It may be noted that no such interaction appears to occur in the tungsten benzyl (3,5-Me₂C₆H₃CH₂)₂W(C₅H₅)₂ [18].

TABLE 1
INTRAMOLECULAR NON-BONDED RADII (Å)

	Cr							
	2.01							
Nb	Mo							
2.07	1.95							
Ta	W	Re	Os	Ir	Pt	Au	Hg ^a	
2.01	1.93				1.78		1.76	

^a Ref. 2.

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