

GEOMETRIES OF AND BONDING IN BI- AND POLYNUCLEAR METAL COMPLEXES WITH BRIDGING LIGANDS

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SUMMARY

The geometries of binuclear and polynuclear complexes of transition and main group metals having bridging groups X (X=halide), OR, SR, NR₂, PR₂, H and R (alkyl, aryl) are discussed. Previous rationales of the bridge stereochemistry in, for example, (BeCl₂)_n and [Be(CH₃)₂]_n are rejected and emphasis is placed on the symmetry of the molecular orbitals and their electron occupancy in electron deficient and electron precise species.

INTRODUCTION

It is a general observation that in many electron deficient compounds such as dimethylberyllium, dimethylmagnesium and trialkyl- and triarylaluminium, the metal-metal separation is close to the sum of covalent radii and that this separation increases considerably in analogous electron precise compounds [2.60 Å in Al₂Me₆¹, 2.70 Å in Al₂Ph₆², 3.40 Å in Al₂Cl₆³; 2.09 Å in (BeMe₂)_n⁴, 2.70 Å in (BeCl₂)_n⁵]. The early discussion of the geometries of dimethylberyllium and beryllium dichloride, which has since obtained general acceptance, argued that the Be-C(Me)-Be bridge bond angle of 66° did not imply metal-metal bonding since it would be "unreasonable" to then expect the Be...Be distance to increase in BeCl₂ as "the electron density in the four membered ring is increased". The acute bridge angles were taken therefore as reflecting a maximum overlap condition between the metal and bridging ligand orbitals⁵.

The recent characterisation of cluster complexes of transition metals with bridging aryl ligands⁶⁻⁹ and the observation of a variety of bridge bond angles and metal-metal separations made us look more closely at these previous explanations; and we now provide a qualitative, symmetry-based theory for the stereochemistries of polynuclear complexes which emphasises the importance of metal-metal interactions. This scheme shows that the earlier remarks need revision.

DISCUSSION

Molecular orbitals and metal-metal bonding in main group compounds

The simple valence bond structure (A) for electron precise molecules has a

counterpart in molecular orbital theory in that the bridging ligand, X, has a filled p orbital parallel to the metal-metal vector which can overlap with metal orbital



(A)

(X = Cl, NR₂, PR₂ etc.
M = main group element)

combinations which are *antibonding* with respect to the two metals (Fig. 1). It is only in the electron deficient compounds that the filled bridge orbitals are *bonding* with respect to the metals; and the additional filled orbitals in electron precise bridged compounds reduce the metal-metal bond order¹⁰.

The intermediate bond angle of 86° for Al-N-Al in Ph₂NAl₂Me₅¹⁰ and the increase in the Al...Al distance compared with that in Al₂Me₆ receives an immediate explanation which is not available from the previous overlap arguments (the metal overlap with nitrogen and carbon hybrid σ -orbitals must be very similar). A similar situation is evident in (BeNMe₂)_n¹¹ *vis à vis* (BeMe₂)_n. It is unfortunate that the geometries of Al₂X₆ compounds (X = Cl, Br or I) are known with such little precision-

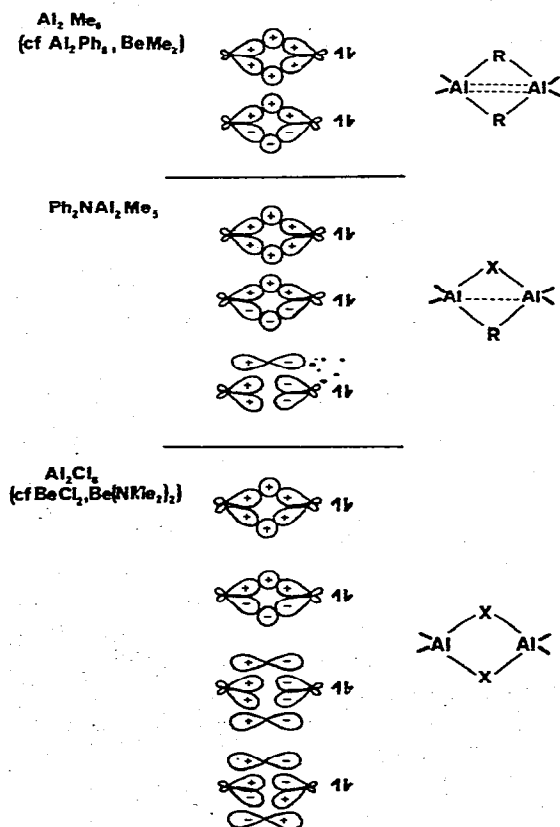
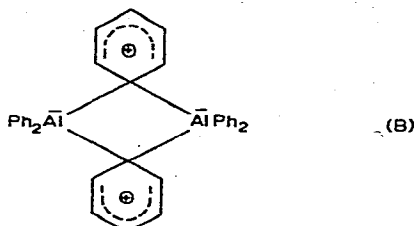


Fig. 1. Bridge molecular orbitals and their occupancy in electron deficient, "half-precise" and electron precise compounds of aluminium.

clearly some variations in the Al–Al distances can be expected to parallel the electronegativity of the bridging halogen and the effective contribution of the ligand p electrons to the bridge MO's. The increase in the aluminium–aluminium distance of ca. 0.1 Å in going from the alkyl to the aryl bridged complexes argues for some p orbital donation from the phenyl ligand π -orbitals, a conclusion not only consistent with the observed conformation of the aryl ring (perpendicular to the Al_2C_2 plane) but also with the intra-ring bond lengths which led Malone and McDonald¹² to suggest a contribution from the resonance structure (B).



One other point should be made which is relevant to our discussion of hydrido bridged complexes of transition metal ions. The simple one electron MO description of diborane implies bonding interactions between the boron atoms; *ab initio* calculations show that *direct* boron–boron overlap is substantial¹³. We do not and cannot distinguish, in general, the cases where a metal–metal bond order is due to direct overlap or to appropriate bridge bonding.

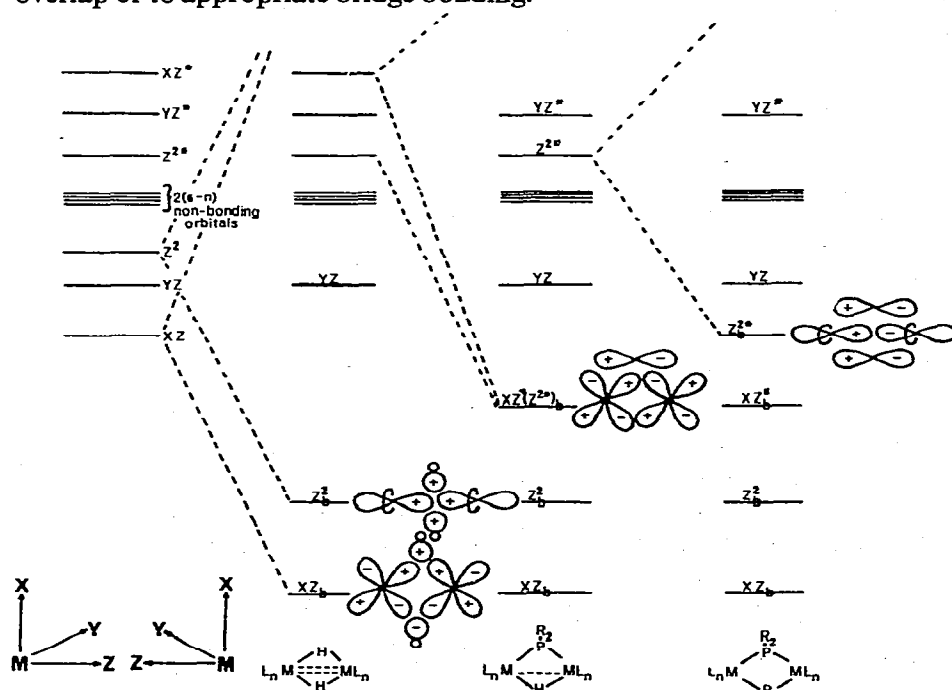


Fig. 2. Schematic molecular orbital scheme for bridged binuclear fragments of transition metal complexes: $Z^2 = 2^{-1}[d_{z^2}(1) + d_{z^2}(2)]$; $Z^{2*} = 2^{-1}[d_{z^2}(1) - d_{z^2}(2)]$ etc., $Z_b^2 = Z^2 +$ appropriate combination of bridging ligand orbitals etc.

TABLE 1

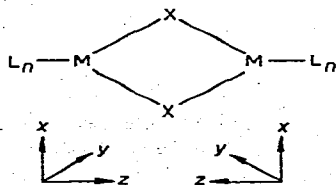
METAL-METAL BOND LENGTHS AND METAL-LIGAND-METAL BOND ANGLES IN SOME BRIDGED COMPOUNDS

Compound	Number	M-M (Å)	M-X-M (°)	Ref.
<i>M-S-M angle^a:</i>				
[Co ₃ (SEt) ₅ (CO)](CO) ₃	1	2.49	67.2	22
[Fe ₂ (CO) ₆ (SEt) ₂]	2	2.54	68.0	23
[Co ₃ (SEt) ₅ (CO)](CO) ₃	3	2.55	69.8	22
[Fe ₂ (SR) ₂ (S ₂ CR) ₄]	4	2.61	72.3	24
[Fe(NO) ₂ (SEt) ₂]	5	2.72	74.0	25
[Fe(π-C ₅ H ₅)(CO)(SMe)] [†]	6	2.93	82.0	26
[Ni(SEt) ₂] ₆	7	2.92	83.0	27
[Fe(π-C ₅ H ₅)(CO)(SPh)] ₂	8	3.39	98.0	14
<i>M-C-M angle^b:</i>				
(Me ₂ Be) _n	1	2.09	66.0	4
[Cu(MeC ₆ H ₃ CH ₂ NMe ₂)] ₄	2	2.38	70.5	8
[(Cu ₂ Br ₂)(CuC ₆ H ₄ NMe ₂) ₄]	3	2.48	75.5	9
Al ₂ Me ₆	4	2.60	75.0	1
(Me ₂ Mg) _n	5	2.72	75.0	28
Al ₂ Ph ₆	6	2.70	77.0	2
[Al ₂ (NPh ₂)(CH ₃)Me ₄]	7	2.72	79.0	10
[Os ₃ (CO) ₈ (PPh ₂)Ph(PPhC ₆ H ₄)]	8	3.10	84.1	6
<i>M-P-M angle^c:</i>				
[Fe(CO) ₄ PdCl(PPh ₂)] ₂	1	2.59	72.3	29
[Co(π-C ₅ H ₅)(PPh ₂)] ₂	2	2.56	72.5	30
[Os ₃ (CO) ₇ (PPh ₂) ₂ (C ₆ H ₄)]	3	2.80	73.5	6
	4	2.99	76.5	
[HOs ₃ (CO) ₇ (PPh ₃)(PPh ₂)(C ₆ H ₄)]	6	2.89	75.0	7
[Os ₃ (CO) ₈ (PPh ₂)(Ph)(PPhC ₆ H ₄)]	7	3.11	82.8	
[Mn ₂ (CO) ₈ (PPh ₂)H]	5	2.94	80.0	18
[Mo ₂ (CO) ₄ (π-C ₅ H ₅) ₂ (PMe ₂)H]	8	3.26	84.7	31
{Cu(PPh ₂)[1,2-(Ph ₂ P) ₂ C ₂ H ₄]} ₂	9	3.34	89.7	32
[Ni(π-C ₅ H ₅)(PPh ₂)] ₂	10	3.36	102.4	30
[Fe(CO) ₃ (PMe ₂)I] ₂	11	3.59	102.4	33

^a See Fig. 3a. ^b See Fig. 3c. ^c See Fig. 3b.

Transition metal complexes

The extension of these ideas to transition metal complexes requires that we introduce some reasonable assumptions. With the coordinate axis system (C) three metal hybrid orbitals, which transform in the same sense as d_{z^2} , d_{xz} and d_{yz} , will form



the most stable bridge molecular orbitals. The monodentate ligands, L_n , will form n stable molecular orbitals with the metal orbitals and the remaining $[9 - (n + 3)]$ metal orbitals can, to a first approximation be regarded as non-bonding. Figure 2 shows that the d_{xz} and d_{yz} orbitals contribute to molecular orbitals which are entirely analogous to those suggested for the electron deficient and electron precise complexes of Fig. 1. The d_{yz} orbital is orthogonal to the M_2X_2 plane and can form bonding and antibonding combinations with the ligand orbitals perpendicular to the M_2X_2 plane.

Whereas hydrido- and alkyl-bridged complexes of main groups elements have short metal-metal distances which may increase on substitution by halo-, phosphido- and amido-bridging groups, the situation in transition metal complexes additionally

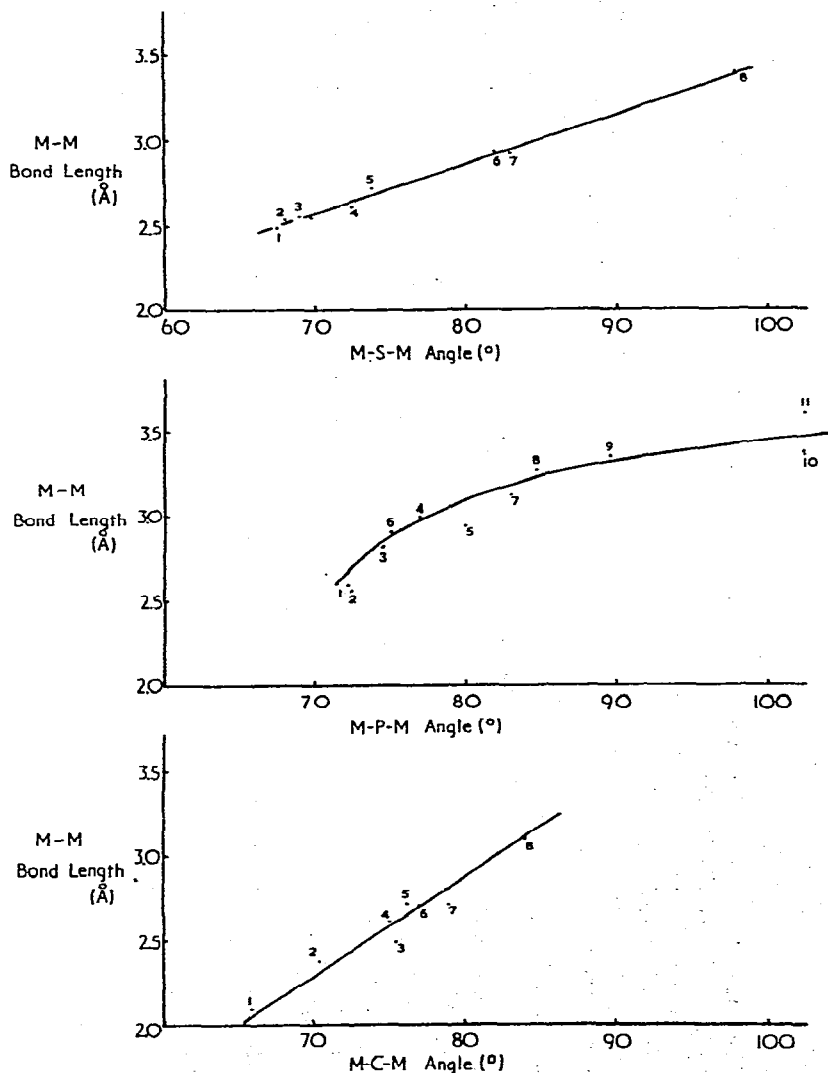


Fig. 3. Metal-metal bond lengths and metal-ligand-metal bridge bond angles for (a) μ -mercapto complexes, (b) μ -phosphido complexes and (c) alkyl and aryl bridged compounds and complexes (see Table 1).

TABLE 2

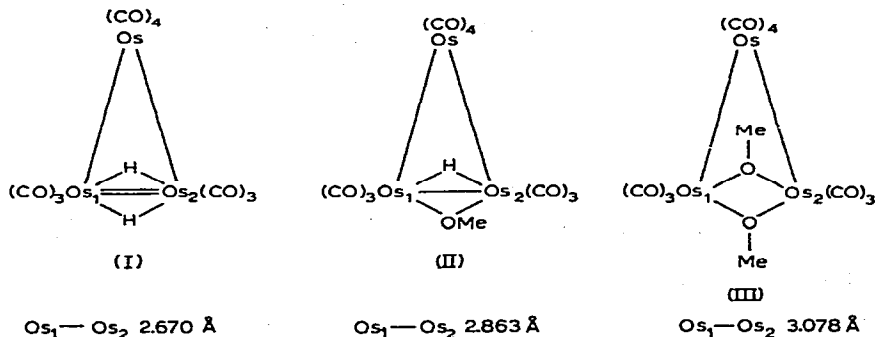
ELECTRONIC CONFIGURATIONS, FORMAL METAL-METAL BOND ORDERS AND METAL-METAL BOND LENGTHS IN SOME BINUCLEAR TRANSITION METAL COMPLEXES

	5	4	3	2
No. of ancillary ligands (n) ^a	5	4	3	2
Electronic configuration	(non-bonding) ⁴ 1	$(XZ_b)^2(Z_b^*)^2(XZ_b^*)^2(Z_b^{*2})^2(YZ)^2$ (non-bonding) ⁸ 1	(non-bonding) ¹² 1	(non-bonding) ¹⁶ 1
Approximate bond order	1	1	1	1
Example	$[(\pi-C_4H_4)MoBr(CO)]_2$	$[Cr(\pi-C_3H_3)(NO)(SR)]_2$	$[Co(\pi-C_3H_3)(PR_2)]_2$	$[Fe(NO)_2(SR)]_2$
Metal-metal bond length	2.95 Å	2.95 Å	2.56 Å	2.72 Å
Electronic configuration		$(XZ_b)^2(Z_b^*)^2(XZ_b^*)^2(Z_b^{*2})^2(YZ)^2$ (non-bonding) ⁸ (YZ*) ² 0	(non-bonding) ¹² (YZ*) ² 0	(non-bonding) ¹⁶ (YZ*) ² 0
Approximate bond order		0	0	0
Example		$[(\pi-C_3H_3)Fe(CO)(SPh)]_2$	$[Ni(\pi-C_3H_3)(PR_2)]_2$	$[Co(NO)_2Cl]_2$
Metal-metal bond length		3.39 Å	3.36 Å	3.20 Å

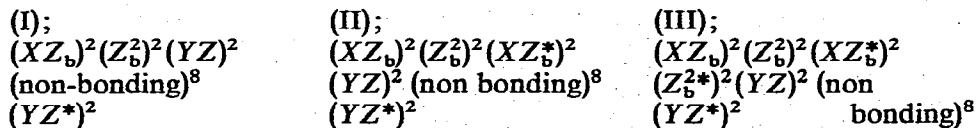
^a $(\pi-C_3H_3)^-$ forms three strongly bonding MO's with metal orbitals.

reflects the electronic configuration of the metal. For example, the metal-metal distance in $\{(\pi\text{-C}_5\text{H}_5)\text{Fe}(\text{CO})(\text{SPh})\}_2$ is 0.44 Å longer than that in $[(\pi\text{-C}_5\text{H}_5)\text{Cr}(\text{NO})(\text{SPh})]_2$ ^{14,15} although the bridging groups are identical. In each case four metal-"terminal" ligand molecular orbitals are formed so that initially there will be two non-bonding orbitals on each metal atom. The electronic configuration of the chromium, according to the scheme of Fig. 2, is $(XZ_b)^2(Z_b^2)^2(XZ_b^*)^2(Z_b^{2*})^2(YZ)^2$ (non-bonding)⁸ whereas it is $(XZ_b)^2(Z_b^2)^2(XZ_b^*)^2(Z_b^{2*})^2(YZ)^2$ (non-bonding)⁸ $(YZ^*)^2$ in the iron complex. The YZ^* orbital is antibonding with respect to the metals and the increase in metal-metal bond length is accounted for. However, we note that YZ^* is non-bonding with respect to the sulphur p - π orbitals and that the S-S distance and the M-S bond lengths should be independent of the metal configuration; in other words, the metal-metal bond lengths and the M-S-M bond angles in a variety of complexes should correlate well. Figure 3 illustrates this correlation and also shows equivalent data for phosphido- and for alkyl- and aryl-bridged complexes of main group and transition elements; we conclude that the metal-metal bond length, which is decided to a large extent by the electronic configuration of the metal, plays the decisive role in determining the M-X-M bond angle and that the size of X is relatively unimportant. Other examples of bridged complexes and a rationalisation of their geometries according to the scheme given in Fig. 2 are listed in Table 2. It should be emphasised perhaps that the presence of suitable metal orbitals (d_{yz}) which can overlap in a plane perpendicular to the MXM plane accounts for the difference in behaviour of transition metal and main group metal bridged compounds.

Our series of complexes that deserves special comment are the trinuclear complexes (I-III)



Simple valence bond arguments based on the rare gas "rule" suggest that the bond orders for $\text{Os}_1\text{—Os}_2$ in these complexes should be 2, 1 and 0 respectively¹⁶. Figure 2 allows us to write the electronic configuration as:



Substitution of a bridging hydride ligand by PPh_2 , SEt or OEt provides two additional electrons in a p_x orbital which can form a stable bonding MO (XZ_b^*) with an antibonding combination of metal XZ orbitals (Fig. 2). Substitution of the two

hydride ligands results in the occupation of three bonding and three antibonding metal-metal bonding orbitals and corresponds roughly to the rare gas rule prediction of zero bond order. The bonding scheme for the dihydride complex suggests that there are two resultant molecular orbitals which are bonding between the metals.

There is a more dramatic distinction for those binuclear complexes of formal metal-metal bond order 1 and 0. For example, the Mn-Mn bond length is approximately 0.8 Å longer in $\text{Mn}_2\text{Br}_2(\text{CO})_8$ ¹⁷ than that in $\text{Mn}_2\text{H}(\text{PPh}_2)(\text{CO})_8$ ¹⁸. The metal-metal bond length in $\text{Mn}_2\text{H}_2(\text{CO})_8$ is not known but the bond length of 2.98 Å in $\text{Re}_2\text{H}_2(\text{CO})_8$ ¹⁹ suggests that it will be significantly shorter than that in the monohydrido complex.

For closely related bridge complexes with the same formal bond order the metal-metal distance is also very dependent on the nature of the bridging groups, the metal-metal bond length decreases with the electronegativity of the bridging group, as the following bond lengths indicate^{15,20,21}:

$\text{Fe}_2(\text{CO})_6(\text{SEt})_2$	2.54 Å	$\{\text{Cr}(\text{NO})(\pi\text{-C}_5\text{H}_5)(\text{SPh})\}_2$	2.95 Å
$\text{Fe}_2(\text{CO})_6(\text{NH}_2)_2$	2.40 Å	$\{\text{Cr}(\text{NO})(\pi\text{-C}_5\text{H}_5)(\text{NMe}_2)\}_2$	2.70 Å
$\text{Fe}_2(\text{NO})_2\text{I}_2$	3.05 Å		
$\text{Fe}_2(\text{NO})_2(\text{SEt})_2$	2.72 Å		

Some concluding remarks

The essential argument presented here is based on symmetry considerations only, a feature which is, at once, a point of weakness and strength. We are pessimistic, at present, of the prospect of carrying out realistic molecular orbital calculations designed to comment upon the extent of involvement of individual ligand orbitals in the various bridge orbitals and have to be satisfied, therefore, with our *ex-post facto* conclusions.

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