

To tilt or not to tilt? The dilemma of $\mu\text{-C}_3\text{R}_3$ ligands in binuclear complexes

Eluvathingal D. Jemmis* and Bharatam V. Prasad

School of Chemistry, University of Hyderabad, Central University P.O., Hyderabad 500 134 (India)

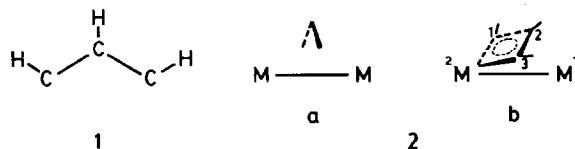
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Abstract

The symmetrical or tilted positioning of $\mu\text{-C}_3\text{R}_3$ groups that straddle an otherwise symmetrical metal–metal bond is dictated by the geometric flexibility available to the terminal ligands of the metal. The C_3Cl_3 in $[(\text{OC})\text{Ni}(\mu\text{-C}_3\text{Cl}_3)\text{Ni}(\text{CO})]_2\text{Cl}_2$ is symmetrical because the $\text{Ni}(\text{CO})\text{Cl}$ groups are free to pyramidalize around the metal so that both metals can bond simultaneously with the bridging ligand. The additional bridging CR group in $\text{L}_2\text{W}(\mu\text{-CR})(\mu\text{-C}_3\text{R}_3)\text{WL}_2$ prevents substantial pyramidalization at the WL_2 centre. In unsymmetrical metal environments the middle carbon of the C_3R_3 group tilts toward the ML_n fragment that provides the more diffuse frontier orbitals. For example, $(\eta^5\text{-C}_5(\text{C}_6\text{R}_5)_2)\text{Ni}(\mu\text{-C}_3(\text{C}_6\text{H}_5)_2)\text{Ni}(\eta^4\text{-C}_4(\text{C}_6\text{H}_5)_4)$ has the middle CR group tilted towards $(\eta^4\text{-C}_4(\text{C}_6\text{H}_5)_4)\text{Ni}$.

Introduction

Though unstable as an isolated species, the C_3R_3 unit as in **1**, can be stabilized as a ligand in transition metal complexes [1–4]. In binuclear complexes the C_3R_3 acts as a bridging ligand, that straddles the metal–metal bond, as in **2** [2–4]. The bridging C_3R_3 is symmetrical (**2a**) in some of the binuclear complexes [3], while in



others the C_3R_3 unit is tilted towards one of the metals (**2b**) [2,4]. This tilting of the bridging ligand is to be expected when the two metals are not the same or when the metal environments are otherwise unsymmetrical [2]. The appearance of C_3R_3 group in an unsymmetrical bridging position in some complexes which are otherwise symmetrical is unexpected. We study this problem here. Our analysis is supported by Extended Hückel calculations [5].

Table 1
Structural details of the binuclear complexes with bridging C_3R_3 ligands studied by diffraction methods

Molecule	M(1)C(2)/M(2)C(2) ^a	θ ^b	ϕ ^b	Terminal LML angle ^b	C(1)-C(2) ^b	References
$[(OC)_2Ni(\mu-C_3Cl_3)(\mu-Cl)]_2$	1.93/1.93	99.7	124.0	96.9	1.40	3a, 3b
$(CNBu^t)_2Pt[\mu-C(C_6H_5)_2COC(C_6H_5)_2]Pt(CNBu^t)$	2.48/2.50	99.0		95.6	1.43	3c, 3d
$(CO)_2(\eta^5-C_3H_5)_2W[\mu-C(C_6H_4Me-4)COC(C_6H_4Me-4)]W(CO)_2(\eta^5-C_3H_5)$	2.64/2.65	98.0			1.53	3e
$(Me_3SiCH_2)_2W[\mu-C(Ph)C(SiMe_3)][\mu-C(SiMe_3)W(CH_2SiMe_3)_2]$	2.45/2.68	106.0	129.5	101.7	1.41	4a, 4b
$(O-i-Pr)_2W[\mu-CHCHC(SiMe_3)][\mu-C(SiMe_3)W(O-i-Pr)_2]$	2.23/2.72	100.9	124.8	102.4	1.42	4b
$(CO)_2(\eta^5-C_3H_5)_2W[\mu-C(C_6H_4Me-4)C(Me)C(Me)]Fe(CO)_3$	2.10/	101.9	126.3		1.44	2a, 2b
$(CO)_2(\eta^5-C_3H_5)_2W[\mu-C(C_6H_4Me-4)C(Ph)C(Ph)]Rh(\eta^5-C_3H_5)$	2.14/	101.2	126.0		1.44	2c
$(CO)_2(\eta^5-C_3H_5)_2Mo[\mu-C(C_6H_4Me-4)C(OMe)C(OMe)CH]Fe(CO)_3$	2.17/				1.41	2j
$(CO)_2(\eta^5-C_3H_5)_2W[\mu-C(CO_2Me)C(CO_2Me)CO]W(\eta^5-C_3H_5)(CO)_2$	2.22/	103.4			1.45	2g
$(\eta^5-C_3H_5)_2Rh[\mu-C(CF_3)C(CF_3)CO]Rh(\eta^5-C_3H_5)$	2.17/				1.44	2h
$(CO)_2(\eta^5-C_3H_5)_2Mo[\mu-C(Me)C(Me)CO]Ni(\eta^5-C_3H_5)$	2.29/	99.9				2i
$(\eta^5-C_5(C_6H_5)_5)Ni[\mu-C_3(C_6H_5)_3]Ni(\eta^5-C_5(C_6H_5)_4)$	2.11/2.44				1.41	2k
$(O_2C_2H_7)Pd[\mu-C_3(C_6H_4OMe-4)_3[\mu-C_3(C_6H_4OMe-4)]Pd(O_2C_2H_7)]$	2.32/2.58	97.5	133.1	89.1	1.41	2l, m

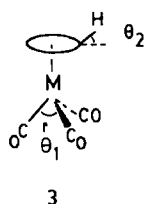
^a The metal that is closer to C(2) is labelled as M(1) (2b). M(2)C(2) values are not reported in some unsymmetrical bridging structures. ^b Average value. Distances are in Å. Angles are in degrees.

A list of binuclear complexes with bridging C_3R_3 group that have been studied by X-ray crystallography is given in Table 1. The ratio M_1C_2/M_2C_2 indicates the extent of tilting of the C_3R_3 group (1, 2). Clearly there are complexes with various degrees of C_3R_3 tilting. However the geometric parameters of the C_3R_3 unit (bond lengths and bond angles, Table 1) remain more or less constant. Even the slightest deviation in the environment of the two metals, as in $(\eta^4-C_4R_4)Ni(\mu-C_3R_3)Ni(\eta^5-C_5R_5)$, leads to the tilting of the C_3R_3 bridge, [2k]. Are there any electronic reasons for the tilting of the central carbon of the C_3R_3 towards $Ni(\eta^4-C_4R_4)$ rather than towards $Ni(\eta^5-C_5R_5)$? The simplest explanation that has been offered for tilting [2k] is that when the C_3R_3 group straddling the M-M bond cannot have effective bonding with both the metals, tilting helps in increasing the binding to one of them. If this is correct, we would like to know how the bonding increases with tilting and what controls the direction of the tilt.

We provide an explanation for the observed geometries based on the diffuse nature and the directionality of the frontier molecular orbitals of the fragments involved. A summary of the understanding of the extension in space of the frontier molecular orbitals is given first. This is used to explain the structure of $(C_4R_4)Ni(\mu-C_3R_3)Ni(C_5R_5)$ and other unsymmetrical bimetallic systems. A study of the symmetric M_2L_4 fragments, one with symmetrical and another with tilted $\mu-C_3R_3$ ligands, follows next. A comparison of these provides useful insights.

The directionality and the extension in space of ML_n and $M(C_nH_n)$ frontier molecular orbitals

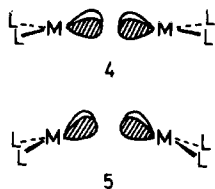
Considerable information is available about the nature of the frontier orbitals of ML_n fragments as a function of L. The number, symmetry properties, energy and extent in space of frontier orbitals of ML_n fragments determine their interaction with other ligands completing the metal coordination sphere, [6]. For example, the frontier MOs of $(\eta^n-C_nH_n)M$ become more diffuse as the value of n decreases. The origin of this effect has been manifested in the increasing $(CO)M(CO)$ angle, θ_1 , in $(\eta^n-C_nH_n)M(CO)_3$ complexes as a function of decreasing n as in 3. The angles are



n	3	4	5	6
M	Co	Fe	Mn	Cr
θ_1	104.0°	97.0°	92.0°	88.0°
θ_2	25.0°	6.0°	0.0°	-3.0°

88° [$n=6$, $C_6H_6Cr(CO)_3$] [7a], 92° [$n=5$, $C_5H_5Mn(CO)_3$] [7b], 97° [$n=4$, $C_4Me_4Fe(CO)_3$] [7c], 104° [$n=3$, $C_3Ph_3Co(CO)_3$] [7d]. The attempts by smaller, rings to optimize their interactions with the metal results in the observed variation in θ_2 as a function of ring size [6]. It is as if the direction of three ligands in an octahedron controls the direction of the remaining three ligands. Thus $(\eta^4-C_4H_4)Ni$ has more diffuse orbitals than $(\eta^5-C_5H_5)Ni$.

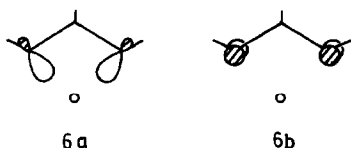
A similar situation exists even in binuclear transition metal templates. The highest lying d orbitals of the L_2MML_2 fragments are the $d_{yz}-d_{yz}$ combination, as in 4. The directionality of these orbitals can be changed by pyramidalization at the



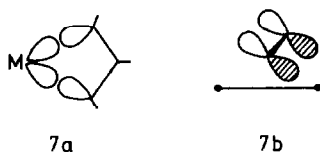
metal. The corresponding orbitals are directed better towards a bridging ligand, as in **5**. We shall see below how such pyramidalizations control metal bridging ligand interactions.

Frontier MOs of C_3R_3 ligand and the structure of $\mu-C_3R_3$ complexes with unsymmetrical metal environments

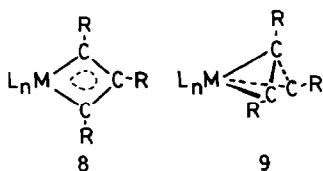
The molecular orbitals of the C_3R_3 ligand have been studied in detail, [8]. Here we point out the differences in the orientation and extension of the σ and π frontier orbitals. The C_3R_3 geometry differs considerably from the standard sp^2 situation. The average internal CCC angle, θ , is decreased to around 100° while the RC(1)C(2) or RC(3)C(2) angle, ϕ , is expanded to around 125° (**1**). The low value of θ is similar to that found in metallacyclobutadienes [1a-i]. The hybrid orbital lobes, which constitute the σ frontier orbitals, are directed towards the M–M bond, as in **6a**. The point at which the M–M bond passes through the C(1)C(2)C(3) plane is



indicated by the circle underneath the carbons. In contrast the p orbitals that constitute the π -MOs of C_3R_3 are parallel to the M–M axis, as in **6b**. Diagrams **7a** and **7b** respectively represent these orbital lobes in the M(2)C(1)C(2)C(3) plane and



as a projection in a plane containing the two metals and the middle carbon of C_3R_3 . The σ - and π -MOs that arise from these individual orbitals will retain these spacial directions. Formally, the C_3R_3 ligand may be treated as a -3 ligand in $L_2W(\mu-C_3R_3)(\mu-CR)WL_2$, so that W is d^1 . This is appropriate for W system which has relatively high AO energies in relation to the MOs of C_3H_3 . This corresponds to allyl anion in the π -frame and two σ hybrid orbitals with two electrons each. Since the molecular orbitals in the σ plane of C_3R_3 will be less diffuse than the π -MOs, the metal fragments with contracted frontier orbitals should prefer bonding in the σ -plane (metallacyclobutadiene), as in **8**. On the other hand metals with more



diffuse frontier orbitals should prefer allyl type of interaction, as in **9**.

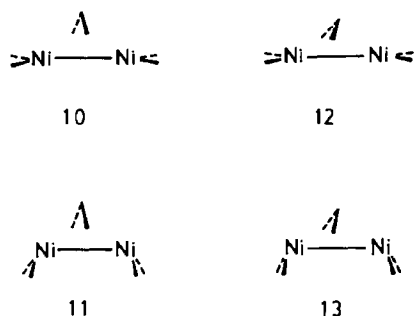
It is natural that the bridging group would not adopt a perpendicular orientation with respect to an M–M bond that does not provide a symmetrical environment. The direction of the tilting should depend on the details of metal– $\mu\text{-C}_3\text{R}_3$ interactions. The orbitals of the tilted C_3R_3 are directed better for a σ -type interaction with one metal and a π -type interaction with the other. The highly directional σ -type MOs (**6a,7a**) overlap better with the metal orbitals that are less diffuse. Consequently the middle carbon of the C_3R_3 will be tilted to the other metal allowing favourable metal–polyene π -interaction. The direction of the tilting then should depend on the terminal ligands on the metal that control the nature of its frontier orbitals.

As discussed above, in $(\eta^5\text{-C}_5\text{Ph}_5)\text{Ni}(\mu\text{-C}_3\text{Ph}_3)\text{Ni}(\eta^4\text{-C}_4\text{Ph}_4)$ ($\eta^4\text{-C}_4\text{Ph}_4$)Ni has more diffuse frontier orbitals than does $(\eta^5\text{-C}_5\text{Ph}_5)\text{Ni}$. Therefore in the binuclear template $(\eta^5\text{-C}_5\text{Ph}_5)\text{Ni}-\text{Ni}(\eta^4\text{-C}_4\text{Ph}_4)$, $(\eta^5\text{-C}_5\text{Ph}_5)\text{Ni}$ should prefer to interact with the σ orbitals of C_3R_3 ; this would bring the central CR group towards the $\text{Ni}(\eta^4\text{-C}_4\text{Ph}_4)$ unit so that it can interact with the π -plane. The X-ray structure of $\text{C}_5(\text{C}_6\text{H}_5)_5\text{Ni}(\mu\text{-C}_3(\text{C}_6\text{H}_5)_3)\text{NiC}_4(\text{C}_6\text{H}_5)_4$ supports this view [2k].

The direction of tilting in the complexes where the two metals are different [2] also can be accounted for by similar arguments. In all such examples noted in Table 1, $\text{CpM}(\text{CO})_2$ fragment provides less diffuse metal orbitals and prefer a σ -type of bonding with the C_3R_3 bridging ligand. The other metal, which in most cases is equivalent to ML_3 , provides more diffuse orbitals for the complex formation and prefers the π -type of bonding with the bridging ligand and so the central carbon of the C_3R_3 group is expected to bend away from the $\text{CpM}(\text{CO})_2$ unit. The X-ray structures clearly show the resulting near planar arrangement of $[(\text{CO})_2\text{Cp}]M\text{C}(1)\text{C}(2)\text{C}(3)$. The crystal structure of $\text{Cp}(\text{CO})_2\text{Mo}[\mu\text{-C}(\text{Ph})\text{C}(\text{OMe})\text{-CH}]\text{Fe}(\text{CO})_3$ shows how pyramidalization at $\text{Fe}(\text{CO})_3$ adjust itself to give more diffuse orbitals [2j]. For example, the $(\text{CO})\text{Fe}(\text{CO})$ angle is below average. In addition, the $\text{Fe}(\text{CO})_3$ unit rotates to adopt a non-sawhorse geometry [9].

Structures of the $\mu\text{-C}_3\text{R}_3$ complexes with symmetrical metal fragments

There are two types of complexes known to have symmetrical binuclear metal fragments and $\mu\text{-C}_3\text{R}_3$ ligands. The first type involves Ni_2 or Pt_2 metals with two terminal ligands each. The second type has a bridging carbyne ligand in addition to the $\mu\text{-C}_3\text{R}_3$ in a W_2 system. In $[(\text{CO})\text{Ni}(\mu\text{-C}_3\text{Cl}_3)\text{Ni}(\text{CO})]_2\text{Cl}_2$ [3a,3b] and $(\text{NCBu}^t)_2\text{Pt}[\mu\text{-C}(\text{Ph})\text{COC}(\text{Ph})]\text{Pt}(\text{NCBu}^t)_2$ [3c,3d] the bridging C_3 unit is perpendicular to the M–M axis. The LML angle in the Ni_2 complex is 96.8° and that in the Pt_2 complex is 95.6° . The environment is pyramidal, with the two ligands bent away from the bridging C_3R_3 group. Interaction diagrams have been constructed for the complex $(\text{CO})_2\text{Ni}(\mu\text{-C}_3\text{H}_3)\text{Ni}(\text{CO})_2^+$ from the smaller fragments $(\text{CO})_2\text{Ni}-\text{Ni}(\text{CO})_2$ and C_3H_3^+ at four different geometries (**10–13**) by use of the fragment molecular



orbital approach within the Extended Hückel method. Figure 1 represents the interaction diagram for the construction of **10**. The bridging of C_3R_3 fragment to the metallic framework primarily stems from three MOs, a_1 , a_2 and b_2 . In addition to these MOs there are MOs resulting from several $4e-2$ orbital interactions. One of these appears in the frontier range (b_2 , HOMO-1). The interaction diagrams for **11**–**13** are similar. The orientation of the orbitals on the metal controls the extent of bonding between the bridging group and the metals. A decrease in LML angle and the pyramidalization at the metal centre (**11,13**) helps in directing the metal orbitals toward the orbitals of C_3R_3 group, and this increases the bonding of the C_3R_3 ligand to both the metals. Table 2 shows the fragment molecular orbital overlap values, corresponding to a_1 and a_2 , between fragments $C_3H_3^+$ and $(CO)_2Ni-Ni(CO)_2$, for complexes **10**–**13**. These values clearly indicate that the larger overlaps are obtained when the allyl group is symmetrical (**10** and **11** > **12** and **13**). Thus symmetrical structures **10** or **11** are more favourable. Further, the maximum overlap occurs in **11** when the C_3R_3 is symmetrical and the CO ligands are bent away from the bridging ligand. Finally, the overlap values between the

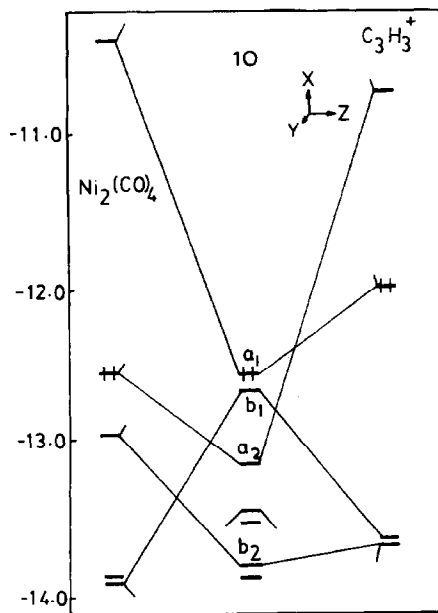


Fig. 1. Interaction diagram for the construction of **10** (C_{2v}). Important orbitals are shown in Fig. 2.

Table 2

Overlap between the fragment molecular orbitals (FMOs) of $(\text{OC})_2\text{Ni}-\text{Ni}(\text{CO})_2$ and C_3R_3 in geometries 10–13

Molecular orbitals	FMO Overlaps			
	10	11	12	13
a_1	0.2809	0.2833	0.2261	0.2358
a_2	0.2305	0.2495	0.1479	0.1621

fragment molecular orbitals of $(\text{CO})_2\text{Ni}-\text{Ni}(\text{CO})_2$ and C_3H_3^+ in geometries 10–13 indicate that structure 11 is most favourable for $(\text{CO})_2\text{Ni}(\mu\text{-C}_3\text{H}_3)\text{Ni}(\text{CO})_2^+$. A Walsh diagram (Fig. 2) for the process 11 \rightarrow 13 indicates that only three orbitals, a_1 , a_2 , b_1 show major change in energy. Bonding combinations a_1 and a_2 rise in energy due to decrease in the bonding nature. The antibonding orbital b_1 falls in energy, but this cannot compensate for the destabilization caused by a_1 and a_2 . As a result, destabilizing interactions predominate the process and 11 is more stable than 13. In the process 10 \rightarrow 12, the a_1 orbital does not show any change, and the changes in the other orbitals are as usual. This indicates that process 10 \rightarrow 12 is less unfavourable. The symmetrical structure is more stable here also. The crystal structure of the two Ni complexes have symmetrical C_3R_3 groups. The freedom available at the terminal ML_2 group for pyramidalization adds to the stabilization of symmetrical structures. If C_3R_3 is taken as a -3 ligand, the nickels will be d^8 with two vacant d orbitals. The C_3R_3 can also be regarded as a $+1$ ligand, in which case Ni will be d^{10} . Charge analysis indicate that actual description should lie somewhere in between. It is difficult therefore to conclude that the $\text{M}-\text{C}_3\text{R}_3$ antibonding MO decreased in energy on tilting by mixing with vacant metal d orbitals.

$\text{L}_2\text{W}(\mu\text{-CR})(\mu\text{-C}_3\text{R}_3)\text{WL}_2$ (d^1-d^1) complexes are examples of the second kind [4a,b]. The major MOs corresponding to $\text{M}-\text{C}_3\text{R}_3$ bonding remain more or less similar to those in Ni_2 or Pt_2 complexes [10a]. It is the restrictions of the terminal ligands that are very different here. The tungsten complexes have two bridging

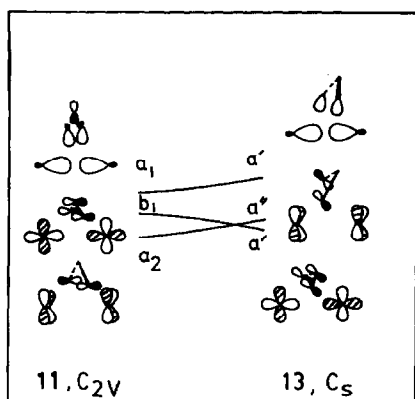


Fig. 2. Walsh diagram for the process 11 (C_{2v}) to 13 (C_s).

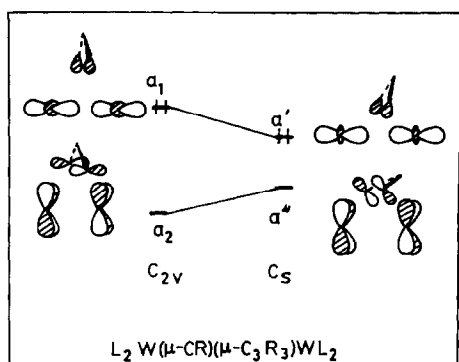


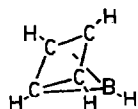
Fig. 3. Walsh diagram for the tilting of C_3R_3 in $L_2W(\mu-C_3R_3)(\mu-CR)WL_2$.

groups (CR and C_3R_3) with opposing requirements on the directionality of the frontier orbitals of the metal. Pyramidalization at the metal in any one direction will have opposite effects on the bridging ligands. The only alternative is to tilt the C_3R_3 group, which allows different terminal LML angles at the metal centres without pyramidalization of the L_2MM unit. This does not increase the stability of tilted structure dramatically. EH calculations for the process $2a \rightarrow 2b$ on the model $(CH_3)_2W(\mu-CH)(\mu-C_3H_3)W(CH_3)_2$ indicate that $2b$ structure is marginally more favourable than $2a$. The HOMO (a_1) is the antibonding combination of a filled–filled interaction and HOMO-1 (a_1) is a bonding combination. On tilting the C_3R_3 group towards one metal, a_1 decreases in energy (Fig. 3). The a_2 orbital increases in energy due to increase in bonding interaction and results in a'' . In this case for $a_1 \rightarrow a'$ decrement in energy is more predominant. On the whole only a slight stabilization arises from the process $2a \rightarrow 2b$. In solution a dynamic equilibrium exists between the two possible tilted geometries even though in the solid state, the C_3R_3 is tilted towards a metal $4b$. Pyramidalization at the metal centres to increase the metal– C_3R_3 bonding in the symmetrical structure is not possible because of the second bridging group, $\mu-CR$.

It should be possible to constrain the terminal ligands in Pt_2 and Ni_2 complexes to force the $\mu-C_3R_3$ group to be unsymmetrical. If the terminal ligands have large bite size and a geometry unable to support pyramidalization at the metal, this should lead to unsymmetrical bridging. Similarly restricting the terminal ligand bite size to small values and forcing pyramidalization at the metal centre as in $[(CO)Ni(\mu-C_3Cl_3)Ni(CO)]_2Cl_2$ and $(NCBu^t)_2Pt[\mu-C(Ph)COC(Ph)]Pt(NCBu^t)_2$ will increase the stability of the complexes with symmetrically bridging C_3R_3 groups.

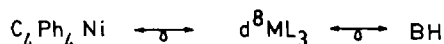
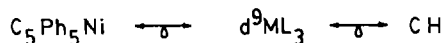
Isolobal analogs of $\mu-C_3R_3$ complexes

The concept of isolobal analogy has increased our understanding of the relationships between organic and inorganic chemistry [11]. We now consider the main group equivalents of the binuclear transition metal complexes, and this will be shown to provide another explanation for the tilting of C_3R_3 structures. We start with $(\eta^5-C_5Ph_5)Ni(\mu-C_3Ph_3)Ni(\eta^4-C_4Ph_4)$. The $(C_5Ph_5)Ni$ group is equivalent to d^8-ML_3 (C_4Ph_4 being regarded as a six-electron dianionic ligand) and isolobal with BH (Scheme 1); thus, the complex is equivalent to C_4H_4BH (**14**). The electron



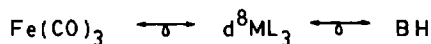
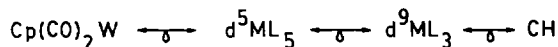
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counting rules for polyhedral molecules indicates that this one must be square-pyramidal [12], while the compatibility of orbitals requires that the BH group be at the apex [13]. Thus the distinction between the frontier orbitals of CpNi and C_4H_4Ni is analogous to that between CH and BH.



Scheme 1

A similar treatment is available for $Cp(CO)_2W(\mu-C_3R_3)Fe(CO)_3$ and related molecules [2b]. The following isolobal changes (Scheme 2) make this compound equivalent to the C_4H_4BH (14) discussed above. This also leads to the expected direction of tilting since BH has more diffuse orbitals.



Scheme 2

Conclusions

A bridging C_3R_3 group in a binuclear transition metal complex will tilt towards one of the metals under two conditions. One of these is the obvious situation where the two metals are not identical or the metal environments are otherwise dissimilar. In this case the C_3R_3 group will tilt towards the metal that provides more diffuse frontier orbitals. This enables the directed σ -type C_3R_3 orbitals to interact with the less diffuse orbitals provided by the other metal. The tilting of the middle carbon of the C_3Ph_3 group towards the $\eta^4-C_4Ph_4Ni$ in $(\eta^5-C_5Ph_5)Ni(\mu-C_3Ph_3)Ni(\eta^4-C_4Ph_4)$ is an example. However, tilted C_3R_3 -bridged complexes are also observed even when the environments are symmetrical. If the directionality of the frontier orbitals of the metal fragments can be increased by pyramidalization at the metal centres metal- C_3R_3 binding can be maintained by both metals equally; thus $(CO)_2Ni(\mu-C_3R_3)Ni(CO)_2^+$ has symmetrically bridging C_3R_3 . However, if such pyramidalizations are not possible for any reason, the bridging group would optimize bonding by tilting. This would lead to specific σ -interactions with one metal and π -interactions to the other. This bending of the terminal ligands is impractical in $L_2W(\mu-C_3R_3)(\mu-CR)WL_2$ because the increase in the binding gained to one bridging group will be cancelled by the loss of binding to the other and this leads to the observed structure in which the C_3R_3 group is tilted towards one metal. Isolobal analogies also lead to similar results.

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Appendix

The geometrical parameters used in the calculations are as follows. Bond lengths (Å): Ni–Ni 2.52, Ni–CO 1.8, C–O 1.14, W–W 2.56, W–CH₃ 2.1, C–H 1.08, C(1)–C(2) = C(2)–C(3) = 1.41. Bond angles (°): C(1)–C(2)–C(3) 100, C–C–H 124, OC–Ni–CO 110, H₃C–W–CH₃ 110. Pyramidalization the Ni in **11** and **13** is achieved by bending the carbonyls down and decreasing the OC–Ni–CO angle from 110 to 98°. The OC–Ni–Ni angles is kept constant in the process. Tilting of the C₃H₃ group is performed so as to get the near planar arrangement of M(2)–C(1)–C(2)–C(3) without altering the geometry of C₃H₃ unit. The M(2)–C(2) distance is increased from 2.52 to 2.70 Å in this process. The M(1)–M(2)–C(2) angle decreased from 60.2 to 54.8°.

References

- R.M. Tuggle and D.L. Weaver, *J. Am. Chem. Soc.*, 92 (1970) 5523; (b) R.M. Tuggle and D.L. Weaver, *Inorg. Chem.*, 11 (1972) 2237; (c) P.D. Frish and G.P. Khare, *Inorg. Chem.*, 18 (1979) 781; (d) J.P. Visser and J.E. Ramakers-Blom, *J. Organomet. Chem.*, 44 (1972) C63; (e) W. Wong, S.J. Singer, W.D. Pitts, S.F. Watkins and W.H. Baddley, *J. Chem. Soc., Chem. Commun.*, (1972) 672; (f) T. Chiang, R.C. Kerber, S.D. Kimball and J.W. Lauher, *Inorg. Chem.*, 18 (1979) 1687; (g) S.F. Pedersen, R.R. Schrock, M.R. Churchill and H.F. Wasserman, *J. Am. Chem. Soc.*, 104 (1982) 6808; (h) M.R. Churchill, J.W. Siller, L. McCullough, S.F. Pedersen and R.R. Schrock, *Organometallics*, 2 (1983) 1046; (i) I.A. Lantham, L.R. Sita and R.R. Schrock, *Organometallics*, 5 (1986) 1508; (j) G. Gervasio, D. Osella and M. Valle, *Inorg. Chem.*, 15 (1976) 1221; (k) S. Aime, D. Osella, A.J. Arce, A.J. Deeming, M.B. Hursthouse and A.M.R. Galas, *J. Chem. Soc., Dalton Trans.*, (1984) 1981; (l) L.R. Beanon, Z.A. Rahman and J.B. Kiestler, *Organometallics*, 2 (1982) 1062; (m) M. Evans, M. Hursthouse, E.W. Randall, E. Rosenberg, L. Milone and M. Valle, *J. Chem. Soc., Chem. Commun.*, (1972) 545; (n) M. Kalam-Alami and R. Mathieu, *J. Organomet. Chem.*, 299 (1986) 363.
 - J.C. Jeffery, K.A. Mead, H. Razay, F.G.A. Stone, M.J. Went and P. Woodward, *J. Chem. Soc., Chem. Commun.*, (1981) 867; (b) J.C. Jeffery, K.A. Mead, H. Razay, F.G.A. Stone, M.J. Went and P. Woodward, *J. Chem. Soc., Dalton Trans.*, (1984) 1383; (c) M. Green, J.A.K. Howard, S.J. Porter, F.G.A. Stone and D.C. Tyler, *J. Chem. Soc., Dalton Trans.*, (1984) 2553; (d) J.C. Jeffery, I. Moore, H. Razay and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1981) 1255; (e) J.C. Jeffery, I. Moore, H. Razay and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1984) 1581; (f) N.M. Boag, R.J. Goodfellow, M. Green, B. Hessner, J.A.K. Howard and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1983) 2585; (g) S.R. Finimore, S.A.R. Knox and G.E. Taylor, *J. Chem. Soc., Chem. Commun.*, (1980) 411; (h) R.S. Dickson, G.S. Evans and F.D. Fallon, *J. Organomet. Chem.*, 236 (1982) C49; (i) M.C. Azar, K.J. Chetutti, C. Eigerbrot and K.A. Green, *J. Am. Chem. Soc.*, 107 (1985) 7209; (j) M.E. Garcia, J.C. Jeffery, P. Sherwood and F.G.A. Stone, *J. Chem. Soc., Chem. Commun.*, (1986) 802; (k) H. Hoberg, R. Krause-Going, C. Kruger and J.C. Sekutowski, *Angew. Chem., Int. Ed. Engl.*, 16 (1977) 183; Few theoretical studies are available on this compound. M.C. Bohm, *Chem. Phys.*, 60 (1981) 277; (l) A. Keasey, P.M. Bailey and P.M. Maitlis, *J. Chem. Soc., Chem. Commun.*, (1977) 178; (m) P.M. Bailey, A. Keasey and P.M. Maitlis, *J. Chem. Soc., Dalton Trans.*, (1978) 1825; (n) A. Keasey and P.M. Maitlis, *J. Chem. Soc., Dalton Trans.*, (1978) 1830.
 - R.G. Posey, G.P. Khare and P.D. Frisch, *J. Am. Chem. Soc.*, 99 (1977) 4863; (b) P.D. Frisch,

- R.G. Posey and G.P. Khare, *Inorg. Chem.*, 17 (1978) 402; (c) W.E. Carroll, M. Green, J.A.K. Howard, M. Pfeffer and F.G.A. Stone, *Angew. Chem., Int. Ed. Engl.*, 16 (1977) 793; (d) W.E. Carroll, M. Green, J.A.K. Howard, M. Pfeffer and F.G.A. Stone, *J. Chem. Soc., Dalton Trans.*, (1978) 1472; (e) J.B. Sehridan, G.L. Geoffroy and A.L. Rheingold, *Organometallics*, 5 (1986) 1514; (f) Formation of symmetric compound $(\eta^5\text{-C}_5\text{H}_5)(\text{OC})_2\text{W}(\mu\text{-CRCOCR})\text{W}(\text{CO})_2(\eta^5\text{-C}_5\text{H}_5)$ is reported in ref. 2c.
- 4 (a) M.H. Chisholm, J.A. Heppert and J.C. Huffmann, *J. Am. Chem. Soc.*, 104 (1984) 1151; (b) M.H. Chisholm, J.C. Huffmann and J.A. Heppert, *J. Am. Chem. Soc.*, 107 (1985) 5116.
- 5 (a) H. Fujimoto and R. Hoffmann, *J. Phys. Chem.*, 78 (1974) 1167; (b) R. Hoffmann and W.N. Lipscomb, *J. Chem. Phys.*, 36 (1962) 2179. R. Hoffmann, *J. Chem. Phys.*, 39 (1963) 1397; (c) Weighted H_{ij} formula used. The EH parameters were taken from D.M. Hoffmann, R. Hoffmann and C.R. Fisel, *J. Am. Chem. Soc.*, 104 (1982) 3858. Geometric parameters are given in the Appendix.
- 6 M. Elia, M.M.L. Chen, D.M.P. Mingos and R. Hoffmann, *Inorg. Chem.*, 15 (1976) 1148.
- 7 (a) B. Rees and P. Coppens, *Acta Crystallogr., Sect. B*, 29 (1973) 2516; (b) A.F. Berndt and R.E. Marsh, *Acta Crystallogr.*, 16 (1963) 118; (c) R.P. Dodge and V. Schomaker, *Acta Crystallogr.*, 18 (1965) 614; (d) T. Chaing, R.C. Kerber, S.D. Kimball and J.W. Lauher, *Inorg. Chem.*, 18 (1979) 1687.
- 8 E.D. Jemmis and R. Hoffmann, *J. Am. Chem. Soc.*, 102 (1980) 2570.
- 9 D.L. Thorn and R. Hoffmann, *Inorg. Chem.*, 17 (1978) 126.
- 10 (a) E.D. Jemmis and B.V. Prasad, *J. Am. Chem. Soc.*, 109 (1987) 2560; (b) M.H. Chisholm, J.A. Heppert, E.M. Kober and D.L. Lichtenberger, *Organometallics*, 6 (1987) 1578.
- 11 (a) M.H. Chisholm, J.A. Heppert, E.M. Kober and D.L. Lichtenberger, *Organometallics*, 6 (1987) 1578.
- 11 (a) R. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, 21 (1982) 711; (b) F.G.A. Stone, *Angew. Chem., Int. Ed. Engl.*, 23 (1984) 89.
- 12 (a) E.D. Jemmis, *J. Am. Chem. Soc.*, 104 (1982) 7017; (b) E.D. Jemmis and P.v.R. Schleyer, *J. Am. Chem. Soc.*, 104 (1982) 4781.
- 13 E.D. Jemmis and P.N.V. Pavan Kumar, *Proc. Ind. Acad. Sci.*, 93 (1984) 479.