Structure and Bonding in $L_2M(\mu\text{-CCR})_2ML_2$ and $L_2M(\mu\text{-RC}_4R)ML_2$ ($L_2M = Cp_2Zr$, Cp_2Ti, R_2Al, $R(NR_3)Be$, (tmpda)Li, H_2B, and H_2C^+). A Molecular Orbital Study

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Abstract: Molecular orbital studies (Extended Hückel and MNDO) have been carried out on models for the title compounds (1–4, $L_2M = H_2Al$, H_2B, H_2C^+, $(NH_3)HBe$, $(NH_3)_2Li$, Cp_2Zr, Cp_2Ti; R = H). When M = Al, Be, or Li the involvement of the π MOs of the bridging acetylene in M–C binding is very small. These lead to structures of the type 1 and 2. The bending of the bridging acetylide group in 2 does not affect this bonding picture. The bonding in boron and carbon analogues can be described by 2c–2e bonding within the four-membered rings, as in 13. $(Cp_2Zr)_2$ or $(Cp_2Ti)_2$ provides an unusually large number of frontier orbitals that are more diffuse and more varied in their symmetry properties. All of them lie in a plane orthogonal to the plane formed by the centroids of the four Cp's. The in-plane π and π^* orbitals of the bridging acetylides find bonding partners among them. Bending the bridging ligand enhances such interactions and lengthens the C–C bond. The two acetylide C atoms (C_1–C_3) develop weak bonding interactions (9). In the Ti complex, the M–C and consequently the C_1–C_3 distances are shorter so that this incipient bonding interaction goes all the way to form the C_1–C_3 coupled product 4. The HC_4H ligand in 4b can be described either as a tetradehydro-*trans*-butadiene or as a zigzag butadiyne. The larger claw-size of the Cp_2M orbitals helps in maintaining optimal CCC angles in 4. Structures corresponding to 4 with main group fragments have been studied with the MNDO method (4: $ML_2 = AlH_2$, BH_2, CH_2^+; R = H). For comparison the pyramidal structure 12, a D_{2h} structure 14, and the planar six-membered ring 15 were also included. 14 was found to be the most stable one among all the isomers so far considered for $C_6H_6^{2+}$. $C_4H_4(BH)_2$ and $C_4H_4(AlH)_2$ were optimized to a stable structure in the geometry 15. Attempts at the synthesis of these species will be rewarding. Isolobal analogy relates 14 to transition-metal complexes such as $CpCo(\mu\text{-CO})_2CoCp$ (16).

With its two orthogonal π bonds available for coordination, acetylene has been a versatile ligand in organometallic chemistry.[1] The two carbon units can be transferred together or separately in forming new C–C bonds.[2,3] The acetylide anion as ligand is equally versatile. The simplest situation involves a linear M–C–C–R arrangement.[4] In binuclear complexes C–C–R appears as a bridging group with a varying degree of bending (1–3, Table I),[5–16] But the other extreme is provided by the complex

(1) (a) Mayer, J. M.; Thorn, D. L.; Tulip, T. H. *J. Am. Chem. Soc.* **1985**, *107*, 7454–7462. (b) Berry, D. H.; Eisenberg, R. *J. Am. Chem. Soc.* **1985**, *107*, 7181–7183. (c) Lee, K.-W.; Pennington, W. T.; Cordes, A. W.; Brown, T. L. *J. Am. Chem. Soc.* **1985**, *107*, 631–641. (d) Lewandos, G. S. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Patai, S., Eds.; Wiley-Interscience: New York, 1982; p 287. (e) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980. (f) Yamamoto, A. *Organotransition Metal Chemistry*; Wiley-Interscience: New York, 1986. (g) Tatsumi, K.; Hoffmann, R.; Templeton, J. L. *Inorg. Chem.* **1982**, *21*, 466–468 and references therein. (h) Cotton, F. A.; Wilkinson, G. *Advanced Inorganic Chemistry*, 4th ed.; Wiley-Interscience: New York, 1983. (i) Kline, E. S.; Kafafi, Z. H.; Hague, R. H.; Margrave, J. L. *J. Am. Chem. Soc.* **1985**, *107*, 7559–7562. (j) For structural data on parallel and perpendicular acetylene complexes, see: Hoffman, D. M.; Hoffmann, R.; Fisel, C. R. *J. Am. Chem. Soc.* **1982**, *104*, 3858–3875.

(2) (a) Hanson, D. M.; Udagawa, Y.; Tohji, K. *J. Am. Chem. Soc.* **1986**, *108*, 3884–3888. (b) Colborn, R. E.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 5470–5477. (c) Reppe, W.; Schichting, O.; Klager, K.; Toepel, T. *Justus Liebigs Ann. Chem.* **1948**, *560*, 1–92. (d) Jolly, P. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 649. (e) Avery, N. R. *J. Am. Chem. Soc.* **1985**, *107*, 6711–6712. (f) Landon, S. J.; Shulman, P. M.; Geoffrey, G. L. *J. Am. Chem. Soc.* **1985**, *107*, 6739–6740. (g) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. In *New Pathways for Organic Synthesis*; Plenum: New York, 1984; p 105. (h) Gentle, T. M.; Muetterties, E. L. *J. Phys. Chem.* **1983**, *87*, 2469–2472. (i) Tysoe, W. T.; Nyberg, G. L.; Lambert, R. M. *J. Chem. Soc., Chem. Commun.* **1983**, 623–625. (j) Sesselman, W.; Woratschek, B.; Ertl, G.; Kueppers, J.; Haberland, H. *Surf. Sci.* **1983**, *130*, 245–258. (k) Nicholas, K. M.; Siegel, J. *J. Am. Chem. Soc.* **1985**, *107*, 4999–5001. (l) Chien, J. C. W. *Polyacetylene: Chemistry, Physics, and Material Science*; Academic: New York, 1984. (m) Bach, R. D.; Wolber, G. J.; Schlegel, H. B. *J. Am. Chem. Soc.* **1985**, *107*, 2837–2841. (n) Baker, G. L.; Schelburne, J. A., III; Bates, F. S. *J. Am. Chem. Soc.* **1986**, *108*, 7377–7380. (o) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539–556. (p) Hirthammer, M.; Vollhardt, K. P. C. *J. Am. Chem. Soc.* **1986**, *108*, 2481–2482. (q) Wakatsuki, Y.; Nomura, O.; Kitaura, K.; Morokuma, K.; Yamazaki, H. *J. Am. Chem. Soc.* **1983**, *105*, 1907–1912. (r) Stockis, A.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2952–2962.

(3) (a) Bencheick, A.; Petit, M.; Mortreux, A.; Petit, F. *J. Mol. Catal.* **1982**, *15*, 93–101. (b) Villemin, D.; Cadiot, P. *Tetrahedron Lett.* **1982**, 5139–5140. (c) Petit, M.; Mortreux, A.; Petit, F. *J. Chem. Soc., Chem. Commun.* **1982**, 1385–1386. (d) Katz, T. J.; McGinnis, J. *J. Am. Chem. Soc.* **1975**, *97*, 1592–1594. (e) Freudenberger, J. H.; Schrock, R. R.; Churchill, M. R.; Rheingold, A. L.; Ziller, J. W. *Organometallics* **1984**, *3*, 1563–1573. (f) Churchill, M. R.; Ziller, J. W.; Freudenberger, J. H.; Schrock, R. R. *Organometallics* **1984**, *3*, 1554–1562. (g) McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 4067–4068. (h) Schrock, R. R. *Acc. Chem. Res.* **1979**, *12*, 98–104. (i) McCullough, L. G.; Schrock, R. R.; Dewan, J. C.; Murdzek, J. C. *J. Am. Chem. Soc.* **1985**, *107*, 5987–5998. (j) Sancho, J.; Schrock, R. R. *J. Mol. Catal.* **1982**, *15*, 75–79. (k) Schrock, R. R.; Pedersen, S. F.; Churchill, M. R.; Ziller, J. W. *Organometallics* **1984**, *3*, 1574–1583. (l) Strutz, H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 5999–6005. (m) Wengrovius, J. H.; Sancho, J.; Schrock, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 3932–3934. (n) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 8, p 499. (o) Devarajan, S.; Walton, D. R. M.; Leigh, G. J. *J. Organomet. Chem.* **1979**, *181*, 99–104. (p) Mortreux, A.; Delgrange, J. C.; Blanchard, M.; Lubochinsky, B. *J. Mol. Catal.* **1977**, *2*, 73–82. (q) Pedersen, S. F.; Schrock, R. R.; Churchill, M. R.; Wasserman, H. J. *J. Am. Chem. Soc.* **1982**, *104*, 6808–6809. (r) Ferudenberger, J. H.; Schrock, R. R. *Organometallics* **1986**, *5*, 1411–1417. (s) Schrock, R. R.; Freudenberger, J. H.; Listeman, M. L.; McCullough, L. G. *J. Mol. Catal.* **1985**, *28*, 1–8.

(4) (a) Weiss, E.; Plass, H. *Chem. Ber.* **1968**, *101*, 2947–2955. (b) Bruce, M. I.; Abu Salah, O. M.; Davis, R. E.; Raghavan, N. V. *J. Organomet. Chem.* **1974**, *64*, C48–C50.

(5) Schubert, B.; Weiss, E. *Chem. Ber.* **1983**, *116*, 3212–3215.

(6) Bell, N. A.; Nowell, I. W.; Coates, G. E.; Shearer, H. M. M. *J. Organomet. Chem.* **1984**, *273*, 179–185.

(7) Morosin, B.; Howatson, J. *J. Organomet. Chem.* **1971**, *29*, 7–14.

(8) Stucky, G. D.; McPherson, A. M.; Rhine, W. E.; Eisch, J. J.; Considine, J. L. *J. Am. Chem. Soc.* **1974**, *96*, 1941–1942.

(9) Almenningen, A.; Fernholt, L.; Haaland, A. *J. Organomet. Chem.* **1978**, *155*, 245–257.

(10) Tecle, B.; Ilsley, W. H.; Oliver, J. P. *Inorg. Chem.* **1981**, *20*, 2335–2337.

(11) Fries, W.; Schwarz, W.; Hansen, H. D.; Weidlein, J. *J. Organomet. Chem.* **1978**, *159*, 373–384.

(12) Atwood, J. L.; Hunter, W. E.; Wyada, A. L.; Evans, W. J. *Inorg. Chem.* **1981**, *20*, 4115–4119.

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$(C_5H_4Me)_4Ti_2C_4Ph_2$ (**4a**), where the two end carbon atoms of the
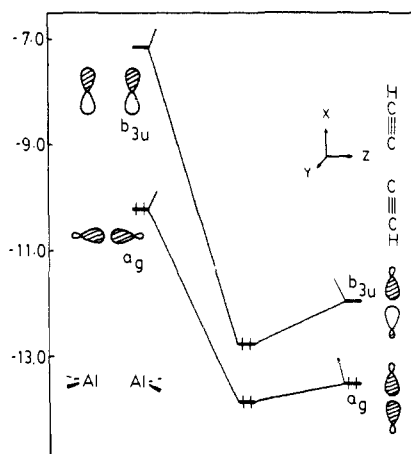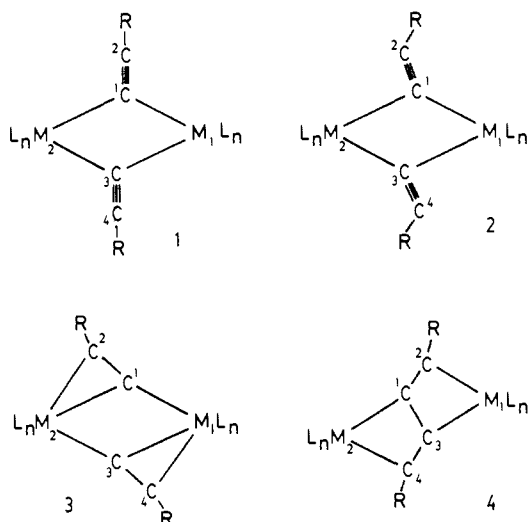
Figure 1. Frontier molecular orbitals of $H_2Al(CCH)_2AlH_2$ obtained from the interaction of the fragments H_2AlAlH_2 and $(CCH)_2$. The π MOs of $(CCH)_2$ are not involved in Al–C bonding.

acetylides have come together to form a conventional C–C (C_1C_3 = 1,485 Å) bond.[17] The binuclear structures with two bridging acetylides for which structural data are available are given in Table I along with their important geometric parameters. The C–C bond length of the acetylide ligand in structures **1** and **2** is very close to that found for the parent alkynes. In **3a**, this distance has been increased to 1.26 Å, as found in $[(C_5H_4Me)_2ZrCCPh]_2$.[16] Interestingly a change of Zr to Ti gives initially the binuclear complex with two bridging acetylides, but eventually it leads to the final product **4a** (Table I).[17,18] The C–C coupled bridging unit, $(RCC)_2$, holds the two Cp_2Ti fragments together. There is no direct Ti–Ti interaction at the observed distance of 4.23 Å. Let us look at the compounds in Table I in greater detail. The various main group fragments [(tmpda)Li,[5] (MeC≡C)-$(NMe_3)Be,$[6] $(Me_3N)(Me)Be,$[7] $Ph_2Al,$[8] $Me_2Al,$[9] $Me_2Ga,$[10] Me_2In[11]] are all isolobal to BH_2 or CH_2^+.[19] We may genuinely worry about the possibility of structures similar to **1** with BH_2 or CH_2^+.

Table I shows that when M is a main group metal the preference for bent structure **2** is not very strong. Thus, the beryllium complex, $Me_3N(Me)Be(CCMe)_2Be(Me)NMe_3$, adopts symmetrical structure **1c**,[7] However, another Be complex Me_3N-$(MeCC)Be(CCMe)_2Be(NMe_3)(CCMe)$ exists in symmetric **1b** and bent **2a** in the same crystal.[6] This shows that the potential energy surface for bending is rather soft. There is no direct correlation between the extent of bending and parameters such as ionic radii or electronegativity of the metal involved. The bending does not affect the C–C distance of the acetylide units in **2**. In fact in the same crystal the bent structure has a shorter C–C distance than that in the symmetrical one (Table I, **2a** vs **1b**),[6] This questions the model of bonding often evoked for these structures.[5-15] If the dimers are formed through the donation of π electrons of one of the acetylide units to the empty orbital on the other metal, the C–C distance should have been longer than that found for the corresponding alkynes.[20] Since bending of the bridged acetylides should help this process of donation of electrons to the metal orbital, we expect long C–C distances, contrary to

the experimental observation. Clearly this means that the acetylenic π MOs are not strongly involved in bridging to the metal in **2**. The situation changes considerably with transition metals. The recently synthesized $[(C_5H_4Me)_2ZrCCPh]_2$ (**3a**) has a C–C bond considerably longer than that found in HC≡CPh.[16] The bridging acetylide group is bent considerably so that the two carbon atoms (C_1 and C_2) are almost equidistant to M_2 (**3a**, Table I). This facilitates π bonding to M_2, while maintaining σ interactions with M_1, resulting in the increased C–C distance. The C_1–C_3 distance involving the two bridges is still longer (3.02 Å) with no indications of any direct C–C bonding. A change of metal works wonders. The isoelectronic $(C_5H_4Me)_4Ti_2C_4Ph_2$ (**4a**) brings the two bridging groups together (C_1C_3 = 1.485 Å), forming a C_4 unit bound from both sides by $(C_5H_4Me)_2Ti$ groups.[17] This ligand may be described as a tetradehydro-*trans*-1,3-butadiene or a zigzag butadiyne. **4a** has been synthesized starting with phenyl acetylide as well as with 1,4-diphenyl-1,3-butadiyne as the ligands.[17]

In the present paper we analyze the electronic structure of the compounds represented by **1–4** and their interconnections. The results also point out the usefulness of the concept of isolobal analogy which is commonly employed in relating complex inorganic structures to those of familiar organic ones.[19] Here we use this analogy at the organic end to find out structures that are overlooked or not normally considered. We start with the analysis of the model compound $H_2Al(CCH)_2AlH_2$ in geometries that parallel **1** and **2**. This is compared to the electronic structure of the models $(C_5H_5)_2M(CCH)_2M(C_5H_5)_2$ (M = Zr, Ti) in the various geometries **1** to **4**. These are carried out within the Fragment Molecular Orbital approach with use of the Extended Hückel theory.[21] The geometries and parameters used are given in the Appendix. Structures **12–15** corresponding to the main group complexes were in addition optimized by the MNDO method so that comparisons can be made to the geometries and energies of species not known experimentally but obtained via isolobal analogy.[22]

Results and Discussion

Electronic Structure of the Main Group Diacetylide Complexes. We construct the molecular orbitals of the symmetric model complex $H_2Al(CCH)_2AlH_2$ starting from the well-known fragments Al_2H_4 and $(CCH)_2$ (Figure 1). The π and π^* MOs are empty in Al_2H_4, while the π as well as the bonding combination of the sp hybrid are occupied in $(CCH)_2$. The major stabilizing interactions are between the two b_{3u} and a_g orbitals resulting in the delocalized σ MOs (labels according to D_{2h} pseudosymmetry)

(13) Evans, W. J.; Bloom, I.; Hunter, W. E.; Atwood, J. L. *Organometallics* **1983**, *2*, 709–714.

(14) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *21*, 957–965.

(15) Corfield, P. W. R.; Shearer, H. M. M. *Acta Crystallogr.* **1966**, *20*, 502–508.

(16) Erker, G.; Fromberg, W.; Mynott, R.; Gabon, B.; Kruger, C. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463–465.

(17) Sekutowski, D. G.; Stucky, G. D. *J. Am. Chem. Soc.* **1976**, *98*, 1376–1382.

(18) Teuben, J. H.; de Liefde Meijer, H. J. *J. Organomet. Chem.* **1969**, *17*, 87–93.

(19) Hoffmann, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 711–724.

(20) Simonetta, M.; Gavezzotti, A. In *The Chemistry of the C–C Triple Bond*; Patai, S., Ed.; John-Wiley: New York, 1978; Part 1.

(21) (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179–2189.

(22) Thiel, W.; Dewar, M. J. S. *J. Am. Chem. Soc.* **1977**, *99*, 4899–4907.

Table I. Experimental Geometric Parameters for **1-4**[a]

molecule, $L_2M(\mu\text{-}CCR)_2ML_2$										
	ML_2	R	M_1M_2	M_1C_1	M_1C_3	C_1C_2	C_1C_2[b]	$M_1C_1M_2$	$M_1C_1C_2$	ref
1a	Li(tmpda)	Ph	2.565	2.132	2.164	1.220	1.188	73.3	143.3	5
1b	Be(NMe₃)(C≡CMe)	Me	2.319	1.836	1.904	1.200	1.204	76.6	154.9	6
1c	Be(Me)(NMe₃)	Me	2.328	1.850	1.890	1.170	1.204	77.0	147.0	7
2a	Be(NMe₃)(C≡CMe)	Me	2.549	1.763	2.042	1.188	1.204	83.8	168.6	6
2b	AlPh₂	Ph	2.999	1.992	2.184	1.207	1.188	91.7	171.6	8
2c	AlMe₂	Me	3.030	2.050	2.153	1.229	1.204	92.0	158.3	9
2d	GaMe₂	Ph	3.196	2.004	2.375	1.183	1.188	86.7	172.8	10
2e	InMe₂	Me		2.193	2.933	1.212	1.204		177.0	11
2f	ErCp₂	CMe₃	3.657	2.420	2.470			96.0	149.0	12
2g	Sm(C₅H₄Me)₂	CMe₃		2.550					151.0	13
2h	Cu(Me₃P)₂	Ph	2.450	1.957	2.073	1.218	1.188	71.5	172.0	14
2l	Ag(Me₃P)₂	Ph	3.033	2.040	2.552	1.208	1.188	81.9	172.9	15
3a	Zr(C₅H₄Me)₂	Ph	3.505	2.188	2.431	1.261	1.188	98.6	187.6	16
4a	Ti(C₅H₄Me)₂	Ph	4.227	2.153	2.325	1.325	1.188			17

[a] Distances are in angstroms and angles are in degrees. [b] C≡C in the corresponding alkynes.[20]

(Figure 1). The π^* of Al_2H_4 is so high that it interacts only with the π^* MOs of CCH. The resulting MO is not occupied. This explains the near constancy of the C–C distance in the acetylide units. There is considerable charge transfer from Al to C as anticipated (1.126e). Since the bonding and antibonding combinations of the sp hybrid orbital are occupied in the complex, the C_1–C_3 Mulliken overlap population is close to zero (–0.057). Similarly the Al–C_4 overlap population is also slightly antibonding (–0.052). At the distance used in these calculations there is hardly any interaction between the Al centers because the coefficient on Al in the two stable MOs is very small (Al–Al Mulliken overlap population is 0.017). The general bonding scheme remains the same for Li, Be, and B compounds with varying degrees of charge transfer.

A Walsh diagram for bending (**1** → **2**) (not shown) the model $H_2Al(CCH)_2AlH_2$ indicates that there is practically no change in the MO energies during this process. The sp hybrid orbital of the bridging CCH is poised for overlap best with one of the Al groups in the bent geometry. Correspondingly the interaction with the second Al decreases. Everything else, including the C–C bonding, remains more or less the same as seen from the overlap populations shown in **5**. The antibonding interaction between Al and C_4 is only slightly reduced (–0.036).
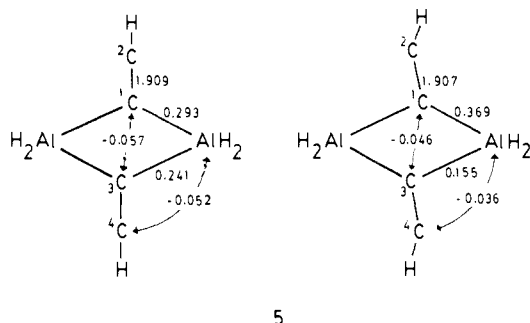
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The flatness of the PE surface for the bending of the CCH group is also seen in the structure of the Be compounds. As mentioned earlier, for the same compound a symmetrically bridging and a tilted structure are found (**1b, 2a**).[6] Minor changes in the ligands around the metal or in the steric requirements of the CCR bridge should control the extent of bending with minimum consequences to the bonding of these complexes. The interaction between the acetylenic bridging carbons (C_1, C_3) remains antibonding even in the bent structure **2**. There seems to be no incipient bonding interaction to trigger the coupling unlike in **4**.

The Electronic Structure of the $(C_5H_4Me)_2Zr(CCH)_2Zr$-$(C_5H_4Me)_2$ Complex. Recently a bis-alkynyl bridging structure involving Cp_2Zr was isolated.[16] This differs from the bridging structures discussed above (**1, 2**) in the following geometric parameters. The C–C bond of the bridging acetylide is substantially longer than that in the parent acetylene (1.26 vs 1.20 Å). The
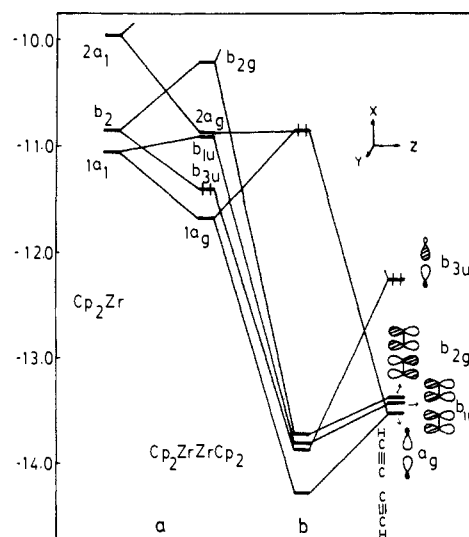
Figure 2. Interaction diagram leading to the molecular orbital energy levels of $Cp_2Zr(CCH)_2ZrCp_2$: (a) $Cp_2ZrZrCp_2$ from Cp_2Zr; (b) the formation of the frontier MOs of $Cp_2Zr(CCH)_2ZrCp_2$ from those of the fragments. Symmetry labels use pseudo-D_{2h} symmetry.
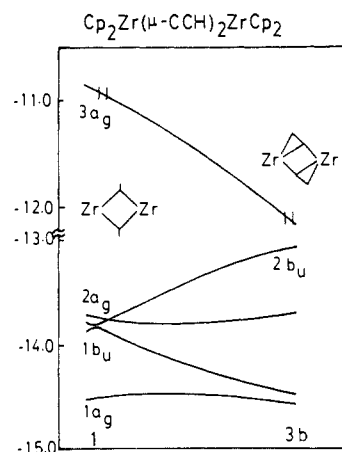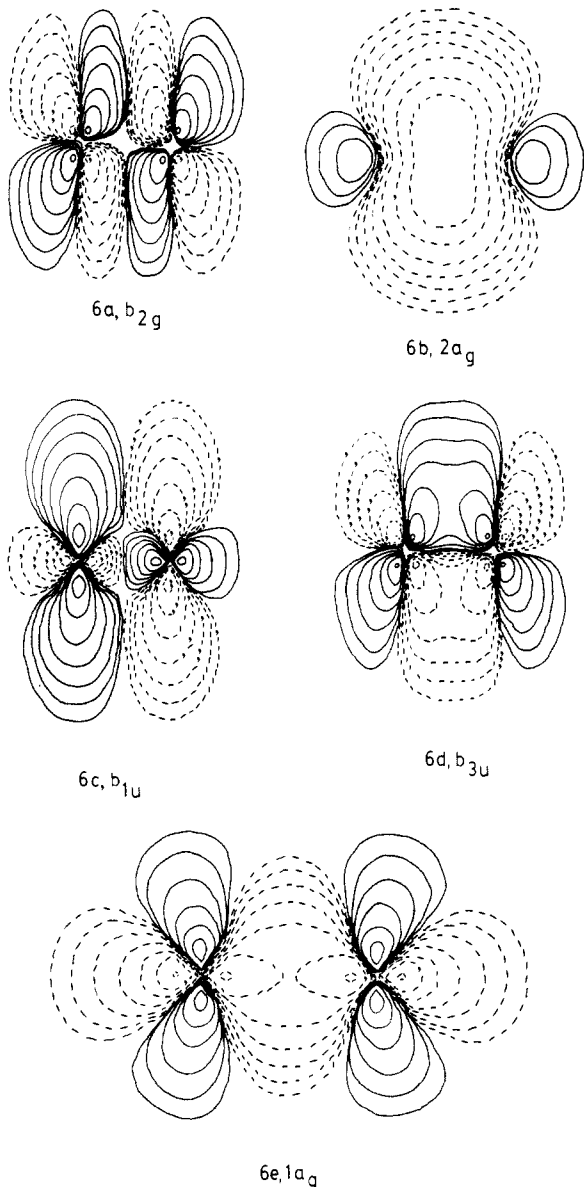
Figure 3. Walsh diagram for the process **1** → **3b** (ML_2 = $ZrCp_2$; R = H).

involvement of the acetylenic π orbitals in the bonding is also indicated by the positioning of the Zr with respect to the acetylide unit. The Zr_2–C_1 and Zr_2–C_2 (**3**) distances are comparable, the latter a shade shorter than the former. **3** represents the skeleton closely. The electronic structure of model compound Cp_2Zr-$(CCH)_2ZrCp_2$ (**3b**) is constructed from the fragments $Cp_2ZrZrCp_2$ and $(CCH)_2$. The frontier orbitals of Cp_2Zr are well docu-

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mented.[23] Two of these groups lead to the MOs of $Cp_2ZrZrCp_2$ shown in Figure 2a.

Electronic Structure of $Cp_2ZrZrCp_2$. The frontier orbitals of Cp_2Zr now lead to a cluster of five MOs with the sixth one going way up in energy. The lowest two orbitals will be occupied in this electron count of d^2-d^2. These MOs can be described as σ $(1a_g)^2$, π $(b_{3u})^2$, σ^* (b_{1u}), δ $(2a_g)$, and π^* (b_{2g}) (symmetry lables are according to the D_{2h} pseudosymmetry of the fragment).

6a, b_{2g}

6b, $2a_g$

6c, b_{1u}

6d, b_{3u}

6e, $1a_g$

Contour plots of **6** show the variety of orbitals, all in one plane, available to $Cp_2ZrZrCp_2$. This provides a basic contrast between the ML_2 (M = main group) and the Cp_2M (M = transition metal) fragments where in addition to the σ and π metal MOs in the bonding range of (C_4H_2) we now have π^* and δ orbitals as well, considerably increasing the possibility of bonding with C_4H_2. An interesting aspect is that all frontier orbitals lie in the xz plane, away from the sterically demanding Cp units. The flexibility available for bonding should lead to a rich chemistry for the $Cp_2ZrZrCp_2$ fragment which is slowly unfolding.[16,24,25]

An interaction diagram leading to the hypothetical (pseudo-D_{2h}) $Cp_2Zr(CCH)_2ZrCp_2$ (akin to **1**) is analyzed first (Figure 2b), HOMO **7** is the antibonding combination from a 4 electron–2 orbital interaction. This is obtained by the interaction of $1a_g$ and


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$2a_g$ orbitals of $Cp_2ZrZrCp_2$ with some contribution from the a_g orbital of $(CCH)_2$. Three other orbitals showed stabilization through 2 electron–2 orbital interactions. These three have substantial $(CCH)_2$ ligand contribution. The first one (b_{2g}) is obtained by the interaction of b_{2g} of $(CCH)_2$ with the antibonding combination of d_{xz} (**6a**) orbitals on the metals. The interaction

(26) (a) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346–7355. (b) Tuggle, R. M.; Weaver, D. L. *J. Am. Chem. Soc.* **1970**, *92*, 5523–5524. (c) Tuggle, R. M.; Weaver, D. L. *Inorg. Chem.* **1972**, *11*, 2237–2243. (d) Frisch, P. D.; Khare, G. P. *Inorg. Chem.* **1979**, *18*, 781–786. (e) Wong, W.; Singer, S. J.; Pitts, W. D.; Watkins, S. F.; Baddley, W. H. *J. Chem. Soc., Chem. Commun.* **1972**, 672–673. (f) Chaing, T.; Kerber, R. C.; Kimball, S. D.; Lauher, J. W. *Inorg. Chem.* **1979**, *18*, 1687–1691. (g) Churchill, M. R.; Ziller, J. W.; McCullough, L.; Pedersen, S. F.; Schrock, R. R. *Organometallics* **1983**, *2*, 1046–1048. (h) Gervasio, G.; Osella, D.; Valle, M. *Inorg. Chem.* **1976**, *15*, 1221–1224. (i) Aime, S.; Osella, D.; Arce, A. J.; Deeming, A. J.; Hursthouse, M. B.; Galas, A. M. R. *J. Chem. Soc., Dalton Trans.* **1984**, 1981–1986. (j) Evans, M.; Hursthouse, M.; Randall, E. W.; Rosenberg, E.; Milone, L.; Valle, M. *J. Chem. Soc., Chem. Commun.* **1972**, 545–546. (k) Jeffery, J. C.; Mead, K. A.; Razay, H.; Stone, F. G. A.; Went, M. J.; Woodword, P. *J. Chem. Soc., Dalton Trans.* **1984**, 1383–1391; *J. Chem. Soc., Chem. Commun.* **1981**, 867–868. (l) Green, M.; Howard, J. A. K.; Porter, S. J.; Stone, F. G. A.; Tyler, D. C. *J. Chem. Soc., Dalton Trans.* **1984**, 2553–2559. (m) Jeffery, J. C.; Moore, I.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1981**, 1255–1258. (n) Jeffery, J. C.; Moore, I.; Razay, H.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1984**, 1581–1588. (o) Boag, N. M.; Goodfellow, R. J.; Green, M.; Hessner, B.; Howard, J. A. K.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1983**, 2585–2591. (p) Dickson, R. S.; Evans, G. S.; Fallon, G. D. *J. Organomet. Chem.* **1982**, *236*, C49–C52. (q) Azar, M. C.; Chetcuti, M. J.; Eigenbrot, C.; Green, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 7209–7210. (r) Garcia, M. E.; Jeffery, J. C.; Sherwood, P.; Stone, F. G. A. *J. Chem. Soc., Chem. Commun.* **1986**, 802–804. (s) Hoberg, H.; Krause-Going, R.; Kruger, C.; Sekutowski, J. C. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 183–184. (t) Keasey, A.; Bailey, P. M.; Maitlis, P. M. *J. Chem. Soc., Dalton Trans.* **1978**, 1825–1830. (u) Posey, R. G.; Khare, G. P.; Frisch, P. D. *J. Am. Chem. Soc.* **1977**, *99*, 4863–4865. (v) Frisch, P. D.; Posey, R. G.; Khare, G. P. *Inorg. Chem.* **1978**, *17*, 402–408. (w) Carroll, W. E.; Green, M.; Howard, J. A. K.; Pfeffer, M.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1978**, 1472–1478. (x) Sheridan, J. B.; Geoffroy, G. L.; Rheingold, A. L. *Organometallics* **1986**, *5*, 1514–1515. (y) Chisholm, M. H.; Heppert, J. A.; Huffman, J. C. *J. Am. Chem. Soc.* **1984**, *106*, 1151–1153. (z) Chisholm, M. H.; Huffman, J. C.; Heppert, J. A. *J. Am. Chem. Soc.* **1985**, *107*, 5116–5136. (aa) Jemmis, E. D.; Hoffmann, R. *J. Am. Chem. Soc.* **1980**, *102*, 2570–2575. (ab) Powell, P. In *The Chemistry of the Metal–Carbon Bond*; Hartley, F. R., Satai, P., Eds.; Wiley-Interscience: New York, 1982; p 235. (ac) Lobach, M. I.; Babitskii, B. D.; Kormer, V. A. *Usp. Khim.* **1967**, *36*, 1158–1199 (in Russian). (ad) Wilke, G.; Bogdanovic, B.; Hardt, P.; Heimbach, P.; Keim, W.; Kroner, M.; Oberkirch, W.; Tanaka, K.; Steinriicke, E.; Walter, D.; Zimmermann, H. *Angew. Chem., Int. Ed. Engl.* **1966**, *5*, 151–164. (ae) Tulip, T. H.; Ibers, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 4201–4211. (af) Rosch, N.; Hoffmann, R. *Inorg. Chem.* **1974**, *13*, 2656–2666. (ag) Jemmis, E. D.; Prasad, B. V. *J. Am. Chem. Soc.* **1987**, *109*, 2560–2563. (ah) Jemmis, E. D.; Prasad, B. V. *Organometallics*, submitted for publication. (ai) Churchill, M. R.; Fettinger, J. C.; McCullough, L. G.; Schrock, R. R. *J. Am. Chem. Soc.* **1984**, *106*, 3356–3357.

(27) Jemmis, E. D. *J. Am. Chem. Soc.* **1982**, *104*, 7017–7020.

(23) (a) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729–1742 and references therein. (b) Hoffmann, R.; Thorn, D. L.; Shilov, A. E. *Koord. Khim.* **1977**, *3*, 1260–1264 (in Russian).

(24) Pez, G. P.; Putnik, C. F.; Suib, S. L.; Stucky, G. D. *J. Am. Chem. Soc.* **1979**, *101*, 6933–6937.

(25) Erker, G.; Kruger, C.; Muller, G. *Adv. Organomet. Chem.* **1985**, *24*, 1–39.

Bonding in L₂M(μ-CCR)₂ML₂ and L₂M(μ-RC₄R)ML₂

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between the two b_{1u} orbitals on the fragments leads to the orbital b_{1u} of **3b**. The interaction between the bonding d_{xz} orbitals (b_{3u}) on the metal fragment with the sp (antibonding) hybrid orbital of (CCH)₂ leads to the b_{3u} MO. Even though a separate interaction diagram is constructed for the experimental geometry of Cp₂Zr(CCH)₂ZrCp₂ (**3b**), more direct information for the causes of extreme bent structure is obtained from the Walsh diagram going from symmetric structure **1** to **3** (Figure 3).

Walsh Diagram for 1 → 3 (M = Zr). Three MOs change considerably as we go from **1** to **3b** (Figure 3). Maximum change is brought to the HOMO **8**. The π and π* MOs of the C₂H unit are no longer constrained by symmetry in interacting with most of the Zr orbitals. The result is clearly seen in the new HOMO

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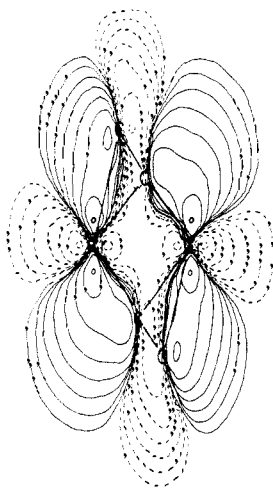
in which Zr is π bonding to one C₂H and σ bonding to the other. This brings down the energy of the HOMO. Bending of the acetylide unit reduces the bonding interaction between Zr₁ and Zr₂ and C₁ and C₂, respectively. This makes 2b$_u$ (since **3b** has only C_{2h} symmetry, the orbitals are labeled according to the C_{2h} point group) go up in energy. The two a$_g$ orbitals 1a$_g$ and 2a$_g$ remain more or less at the same energy level. The obvious conclusions to be drawn from Figure 3 are the following. **3b** (M = Zr) is more stable than symmetric structure **1** (ML₂ = ZrCp₂) and its stability is controlled by the HOMO energy. If we remove two electrons from the system it represents the Sc analogue of **3** (M = Sc). Since the HOMO − 1 energy level is lower in **1**, the Sc analogue should have a type **1** structure. So far it is assumed to be dimeric, based on molecular weight determinations in solution, and no evidence for the structure is known.[28] The increased Zr–acetylide binding is reflected in the Mullilken overlap population values (**9**). There is considerable decrease in the C₁–C₂ population. There is a slight bonding C₁–C₃ interaction that seems to develop already. This does not lead to the formation of a new C–C bond between CCH units with Zr, but it does so with Ti. This process is discussed in the next section.

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(28) Couttis, R. S. P.; Wailes, P. C. *J. Organomet. Chem.* **1970**, *25*, 117–122.
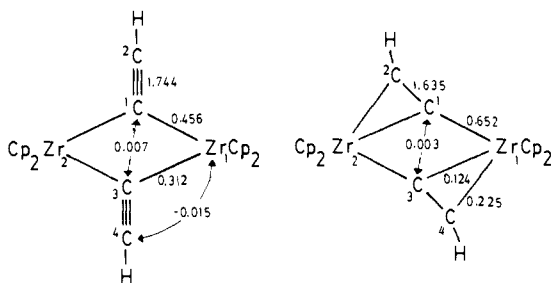
The Electronic Structure of (C₅H₄Me)₂Ti(RC₄R)Ti(C₅H₄Me)₂. Formation of the C–C Bond. The structure of Ti complex **4a** provides several unusual features. The long Ti–Ti distance of 4.23 Å precludes any strong direct metal–metal interaction. The bridging unit is no more the separate acetylides used in the synthesis. The C₁–C₃ coupled bridge may be described as a tetradehydro-*trans*-butadiene or as a bent 1,3-butadiyne. Each Cp₂Ti unit binds to one of the 1,3-carbon sites of the RC₄R ligand. This MC₃ unit resembles the didehydroallyl ligand found in many mono- and binuclear complexes but with an important geometrical difference.[26] The CCC angles in the didehydroallyl complexes are all close to 100° (e.g., Ir(CO)Cl(PR₃)₂(C₃Ph₃)⁺, CCC = 102°). However, the CCC angles in the PhC₄Ph unit are close to 127° (**4a**). This points to the highly diffuse nature of the Cp₂Ti orbital in comparison to those of an ML₄ fragment involving a metal on the right-hand side of the periodic table. The "natural" angle in the didehydroallyl group should be closer to 120° or larger. Maximum bonding interactions take place between MOs that are optimally placed in the fragment geometry itself, without resorting to any distortions.[27] Therefore it is reasonable to anticipate the interaction between the Cp₂M (M = early transition metal) and the C₃R₃ group to be very strong. We could not find any experimental example of such a structure, but derivatives of Cp₂ZrC₃H₃⁺ and Cp₂ScC₃H₃ should present relatively unstrained metallacyclobutenyls and be obtainable in the laboratory. Structures of type **10** (W[C-*t*-BuCMeCMe]Cl₃) were isolated and characterized in the acetylene metathesis reactions.³ᵈ In **10** also the CCC angle is close to 120 (118.9°).
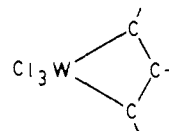

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We have constructed the molecular orbitals of the models Cp₂ZrC₄H₂ZrCp₂ (**3b**) and Cp₂TiC₄H₂TiCp₂ (**4b**) in geometries appropriate for **4**. These are qualitatively similar. Our method cannot provide quantitative differences accurately. We have used the results for Zr in the following discussion. As anticipated when the distance between the two Zr atoms increases to 4.55 Å the interaction between the two Cp₂Zr units decreases. Accordingly, 1a$_g$, b$_{3u}$, 2a$_g$ (bonding orbitals) go up and b$_{2g}$, b$_{1u}$ (antibonding orbitals) come down in energy (Figure 4a). The MOs of HC₄H are obtained from the orbitals of butadiyne (Figure 4b). Only the in-plane π orbitals get mixed with (p$_x$, s), changing their energy (Figure 4b). Three orbitals show major stabilizing interactions (**11**). The HOMO results from the interaction of 1a$_g$ and 2a$_g$ MOs of Cp₂ZrZrCp₂ with the unoccupied 3a$_g$ orbital of C₄H₂ (**11a**). The 2b$_u$ MO is a combination of d$_{xz}$ (bonding) orbitals on the two metals (b$_u$) with the 2b$_u$ orbital of (CCH)₂ (**11b**). The antibonding combination of the metal d$_{xz}$ orbitals (2a$_g$) interacts with 1a$_g$ and 2a$_g$ of (CCH)₂ leading to **11c**. The 1b$_u$ orbital of (CCH)₂ is also stabilized. There are several interactions involving the perpendicular π MOs of the C₄H₂ unit but none contributing substantially to M–C bonding. The 1b$_g$ of (CCH)₂ interacts with the predominantly ligand based orbitals of the metal fragment, but both the bonding and antibonding orbitals are occupied. The bonding patterns for **3** and **4** remain the same for Ti and Zr. Why then does the Cp₂Zr(CCH)₂ZrCp₂ stop at stage **3**? We feel that the larger size of Zr and consequent Zr–C bond lengths (2.303 Å for Zr vs 2.153 Å for Ti) make the C₁–C₃ distance not close enough to get the bond formation going. Titanium in a similar structure brings the C₁–C₃ distance still closer, enhancing the C₁–C₃ bonding already noticed in Zr complex **9**. Probably an extra push by anisotropic application of pressure may force the reaction **3a** → **4** for Zr.

From Inorganic to Organic Chemistry through Isolobal Analogy. One important characteristic of the main group acetylide bridged compounds has been the constancy of the number of electrons. When the metal is shifted from Al to Be to Li, the number of electrons is preserved by replacing the alkyl substituents with two

11a   11b

11c
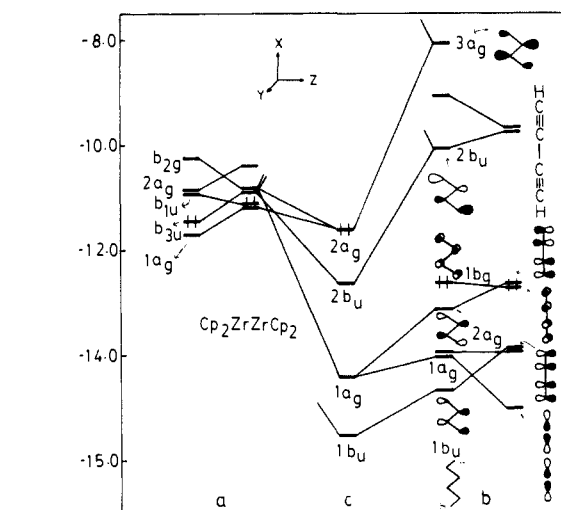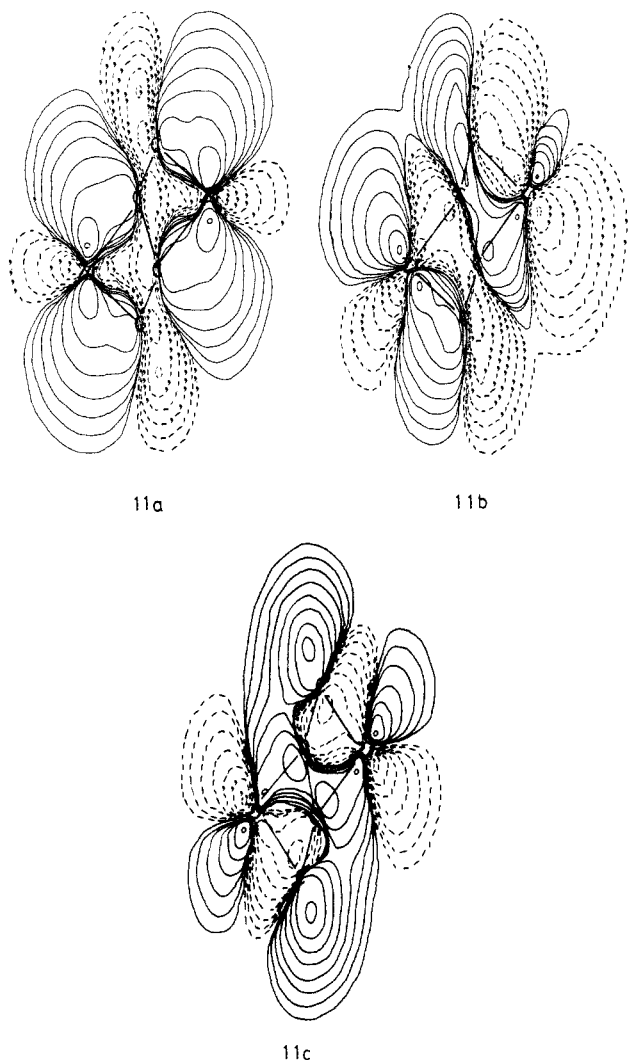
Figure 4. (a) Correlation between the orbitals of $Cp_2ZrZrCp_2$ at 3.5 and 4.5 Å. Only the frontier MOs are shown. (b) Orbitals of bent butadiyne as obtained from the orbitals of linear butadiyne. (c) Orbitals of **4b** (ML_2 = $ZrCp_2$) obtained by the interaction of the MOs of the fragments a and b.

Table II. MNDO Heats of Formation (ΔH_f) for **12-15** (M = B, Al, C^+) and **4** (ML_2 = BH_2, AlH_2, CH_2^+; R = H)[a]

molecule	12	13	14	15	4
$B_2C_4H_6$	56.3	91.3	36.8	19.6	143.5
	(36.7)	(71.7)	(17.2)	(0.0)	(123.9)
$Al_2C_4H_6$	52.2	89.6	38.6	21.9	155.1
	(30.3)	(67.7)	(16.7)	(0.0)	(133.2)
$C_6H_6^{2+}$	649.2[b]	610.7	568.3	571.0[b]	655.1
	(80.9)	(42.4)	(0.0)	(2.7)	(86.8)

[a] Values in the parentheses corresponding to relative stabilities of the various isomers. All values are in kcal/mol. [b] Taken from ref 30a.

electron donor ligands such as NR_3. If one extrapolates to boranes or carbocations the corresponding compounds will be $H_2B(CC-H)_2BH_2$ and $H_2C(CCH)_2CH_2^{2+}$. Compounds corresponding to these molecular formulae have been studied in detail.[29,30] The best known isomer of $B_2C_4H_6$ has a pentagonal pyramidal structure, which follows the six interstitial electron count and the expected positional isomer stabilities.[31] Detailed experimental and theoretical studies of the $C_6H_6^{2+}$ are available but none considered the acetylene bridged structure.[30] Similarly structures equivalent to the coupled $Cp_4Ti_2(C_4H_2)$ complex have not been studied. Such isoelectronic extensions have been extremely fruitful especially in the pyramidal and polyhedral compounds. The pyramidal $C_4B_2H_6$ is found to have its isostructural, isoelectronic analogues in $C_5BH_6^+$,[32] C_5BeH_6,[33] C_5H_5Li,[34] $C_6H_6^{2+}$,[30] and a host

of other structures.[35,36] It is not our intention to present a state of the art, quantum chemical estimate of the structures and relative energies of these species here. We leave it to those with unlimited computational resources. However, we use here the semiempirical MNDO method for obtaining a rough estimate of the structure and energies of main group compounds isolobal to **1-4**. Model compounds corresponding to **1** to **4** where ML_2 = CH_2^+, BH_2, and AlH_2 and R = H were studied by MNDO method. Optimization of the structures gave the following results. Structures **2** and **3** on optimization went back to **1**. Minima were obtained corresponding to **1** and **4**. We have included two other structural types in this study for comparison. The first is the pentagonal pyramidal arrangement **12** found experimentally for M = B and C^+.[29,30b] A second structure for $C_6H_6^{2+}$ surfaced itself from **1** (ML_2 = CH_2^+; R = H) and one of its resonance structures has two bridging vinyl cation groups (**13**). A more stable isomer may be obtained by shifting one of the hydrogens of the CH_2 in **13** to the vinyl cation position resulting in **14**. Corresponding structures for the Al and B analogues were also considered. A thallium analogue is known experimentally with a structure close to **14**.[37] The relative energies are given in Table II.

(29) (a) Groszek, E.; Leach, J. B.; Wong, G. T. F.; Ungermann, C.; Onak, T. *Inorg. Chem.* **1971**, *10*, 2770–2777. (b) Onak, T. P.; Wong, G. T. F. *J. Am. Chem. Soc.* **1970**, *92*, 5226. (c) Miller, V. R.; Grimes, R. N. *Inorg. Chem.* **1972**, *11*, 862–865.

(30) (a) Lammertsma, K.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1983**, *105*, 1049–1051. (b) Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413–420. (c) Giordano, C.; Heldeweg, R. F.; Hogeveen, H. *J. Am. Chem. Soc.* **1977**, *99*, 5181–5183. (d) Hogeveen, H.; Kwant, P. W. *Tetrahedron Lett.* **1973**, 1665–1670. (e) Hogeveen, H.; Kwant, P. W. *J. Am. Chem. Soc.* **1974**, *96*, 2208–2214. (f) Jonkman, H. T.; Nieuwpoort, W. C. *Tetrahedron Lett.* **1973**, 1671–1674. (g) Dewar, M. J. S.; Holloway, M. K. *J. Am. Chem. Soc.* **1984**, *106*, 6619–6627. (h) Appling, J. R.; Burdick, G. W.; Hayward, M. J.; Abbey, L. E.; Moran, T. F. *J. Phys. Chem.* **1985**, *89*, 13–17. (i) Glidewell, C.; Lloyd, D. *Tetrahedron* **1984**, *40*, 4455–4472.

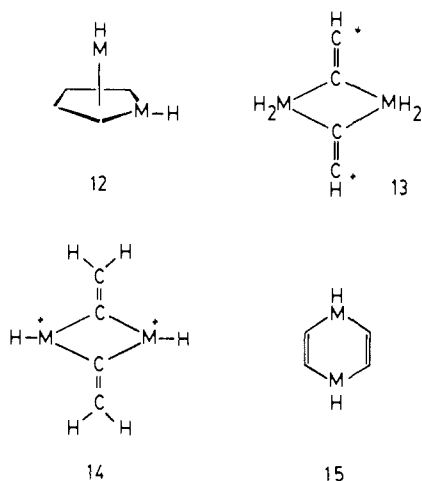(31) Pasinski, J. P.; Beaudet, R. A. *J. Chem. Soc., Chem. Commun.* **1973**, 928–929.

(32) (a) Jutzi, P.; Seufert, A. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 330–331. (b) Jutzi, P.; Seufert, A. *J. Organomet. Chem.* **1978**, *161*, C5–C7. (c) Jutzi, P.; Seufert, A.; Buchner, W. *Chem. Ber.* **1979**, *112*, 2488–2493.

(33) (a) Haaland, A. *Top. Curr. Chem.* **1975**, *53*, 1–23. (b) Drew, D. A.; Morgan, G. L. *Inorg. Chem.* **1977**, *16*, 1704–1708. (c) Gains, D. F.; Coleson, K. M.; Hillenbrand, D. F. *J. Magn. Reson.* **1981**, *44*, 84–88. (d) Drew, D. A.; Haaland, A. *Acta Chem. Scand.* **1972**, *26*, 3079–3084. (e) Bell, N. A. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Eds.; Pergamon: Oxford, 1982; Vol. 1, p 146.

(34) (a) Janoschek, R.; Diercksen, G.; Preuss, H. *Int. J. Quantum Chem.* **1967**, *1*, 205–208. (b) Alexandratos, S.; Streitwieser, A., Jr.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1976**, *98*, 7959–7962. (c) Rhine, W. E.; Stucky, G. D. *J. Am. Chem. Soc.* **1975**, *97*, 737–743. (d) Cox, R. H.; Terry, H. W., Jr.; Harrison, L. W. *J. Am. Chem. Soc.* **1971**, *93*, 3297–3298. (e) Fisher, P.; Stadelhofer, J.; Weidlein, J. *J. Organomet. Chem.* **1976**, *116*, 65–73.
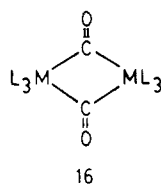
(35) Jemmis, E. D.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1982**, *104*, 4781–4788.

(36) Jemmis, E. D.; Pavan Kumar, P. N. V. *Proc. Indian Acad. Sci. (Chem. Sci.)* **1984**, *93*, 479–489.

Bonding in $L_2M(\mu\text{-}CCR)_2ML_2$ and $L_2M(\mu\text{-}RC_4R)ML_2$

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Theoretical studies at several levels have been carried out on $C_6H_6^{2+}$ previously.[30a,g,35] We find that **14**, which has not been considered previously, is the lowest energy isomer at the MNDO level. Comparisons of relative energies for $C_6H_6^{2+}$ isomers are available at the MNDO and several ab initio levels.[30a] These show that the MNDO estimates are reasonable. Therefore attempts to prepare the dication **14** should be rewarding.[38] **14** is more stable than **12** (M = C⁺) which has been prepared in solution.[30b] What is interesting is that even **13** is more stable than **12** (M = C⁺) by 38.5 kcal/mol at the MNDO level. However, such a large difference may not be realistic as ab initio calculations have shown that the MNDO underestimates the stability of **12** by almost 40 kcal/mol. **4** ($ML_2 = CH_2^+$, R = H) is the least stable of all the isomers. The stability ordering of boron and aluminum analogues is as follows. Al or B analogues of **14** (MH⁺ = AlH or BH) are not the most stable isomers. Both $Al_2C_4H_6$ and $B_2C_4H_6$ gave another minimum corresponding to a six-membered-ring structure, **15** (M = B, Al). The pentagonal pyramidal structures and structures analogous to **14** are the next best out of the other $C_4B_2H_6$ or $C_4Al_2H_6$ isomers considered in this study. It may be possible to prepare a pentagonal pyramidal derivative of $Al_2C_4H_6$.

The extra stability of **14** prompted us to look for isolobal transition-metal fragments. Since CH⁺ is isolobal to the d^8-ML_3 unit, complexes of type **16** should be stable. There are several examples of such compounds, e.g., $CpCo(\mu\text{-}C=O)_2CoCp$.[39] This again shows that one can go back and forth between organic and inorganic realms, modifying structures with the accepted modalities of understanding of either field and obtaining profitable interconnections at each stage with use of isolobal analogy.

Conclusions

Molecular orbital studies using Extended Hückel and MNDO methods on the models for **1–4** (ML_2 = AlH_2, BH_2, CH_2^+, Be-$(NH_3)H$, $Li(NH_3)_2$, $TiCp_2$, $ZrCp_2$; R = H) revealed the following. When M = Al, Be, or Li the π MOs of the bridging acetylide unit do not contribute to the bonding of **1** and **2**. Bending of the bridging acetylide does not affect this bonding in **2**. The in-plane fragment MOs of Cp_2Zr and Cp_2Ti in **3** and **4** enable the acetylenic orbitals to take part in M–C bonding. Bending the bridging acetylides increases the interactions between the metal and acetylide carbons, thereby lengthening the C–C bond. This also initiates weak bonding interactions between the bridging carbon atoms of the two acetylide units, as seen in **9**. With shorter M–C distances this C–C interaction leads to the new C–C bond formation for M = Ti. Isolobal analogy is used in relating **1** (M = Al, Be, Li) to $C_6H_6^{2+}$ and $B_2C_4H_6$. Geometry optimization with MNDO on **1–4** (M = Al, B, C⁺) and **12–15** showed that carbon prefers a structure similar to type **14** and Al and B prefer **15**. Isolobal analogy relates the transition-metal analogue $CpCo(\mu\text{-}CO)CoCp$ to **14**.

Appendix

Parameters for all the atoms used in the Extended Hückel calculations are taken from previous studies (carbon, hydrogen, beryllium, nitrogen, lithium, and aluminium[21] and Zr and Ti[40]). The geometries for the model calculations were based upon the known complexes wherever possible: Al_1–C_1 = 2.053 Å, Al_1–C_3 = 2.153 Å, Al–Al = 3.030 Å, C_1–C_2 = 1.229 Å, Al–H = 1.55 Å, C–H = 1.08 Å were used in $H_2Al(CCH)_2AlH_2$ calculations with 1 and 2 geometries. For **3b**, the experimental distances, i.e., Zr_1–C_1 = 2.188 Å, Zr_1–C_3 = 2.431 Å, Zr_1–C_4 = 2.407 Å, Zr–Zr = 3.505 Å, C_1–C_2 = 1.261 Å, Zr–C_{Cp} = 2.473 Å, C_{Cp}–C_{Cp} = 1.365 Å, and C–H = 1.08 Å were used. The calculations were done with the following distances for **4b** (M = Zr): Zr_1–C_1 = 2.475 Å, Zr_1–C_2 = 2.231 Å, Zr_1–C_3 = 2.303 Å, and C_1–C_3 = 1.485 Å. For Ti calculations, a difference of 0.15 Å is taken from the observed Zr–C distances. Other parameters were adopted accordingly. Distances involving other main group elements are Be–C = 1.836 Å, Be–N = 1.766 Å, Li–C = 2.132 Å, and Li–N = 2.115 Å, respectively.

Supplementary Material Available: Complete specifications (Z matrices and Cartesian coordinates) of the geometries of **12–15** and **4** (M = B, Al, C⁺) (7 pages). Ordering information is given on any current masthead page.

(37) Uemura, S.; Miyoshi, H.; Okano, M.; Ichikawa, K. *J. Chem. Soc., Perkin Trans. 1* **1981**, 991–994.

(38) In a recent study Dougherty et al. discussed the electronic structure of dimethylenecyclobutadiene and its polymers. Removal of the two non-bonding electrons gives the dication **14**, which employs all electrons in bonding. Pranata, J.; Dougherty, D. A. *J. Am. Chem. Soc.* **1987**, *109*, 1621–1627.

(39) (a) Lee, W.-S.; Brintzinger, H. H. *J. Organomet. Chem.* **1977**, *127*, 87–92. (b) Pinhas, A. R.; Hoffmann, R. *Inorg. Chem.* **1979**, *18*, 654–658. (c) Ginsburg, R. E.; Cirjak, L. M.; Dahl, L. F. *J. Chem. Soc., Chem. Commun.* **1979**, 468–470. (d) Bailey, W. I., Jr.; Collins, D. M.; Cotton, F. A.; Baldwin, J. C.; Kaska, W. C. *J. Organomet. Chem.* **1979**, *165*, 373–381. (e) Stephens, F. S. *J. Chem. Soc. A* **1970**, 2745–2748.

(40) Tatsumi, K.; Nakamura, A.; Hofmann, P.; Stauffert, P.; Hoffmann, R. *J. Am. Chem. Soc.* **1985**, *107*, 4440–4451.