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**Supplementary Material Available:** Structure determination summary, tables of atomic coordinates, bond lengths, bond angles, and anisotropic displacement coefficients, and a molecular diagram (8 pages); observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.

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# σ-Hydrocarbyl-Bridged Gallium/Zirconium Complexes Containing Planar-Tetracoordinate Carbon

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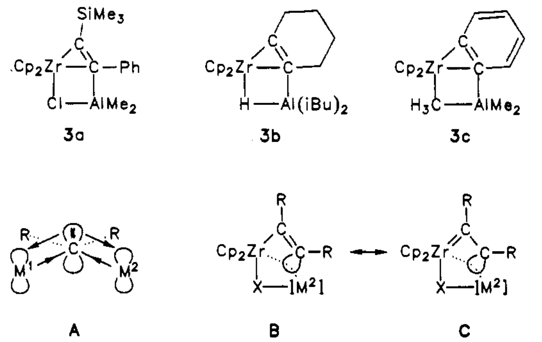
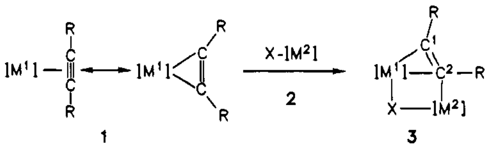
**Abstract:** Several examples are described where in situ generated ($\eta^2$-alkyne) group 4 metallocene type substrates add to X-[$M^2$] reagents ($M^2$ = main group metal) to form dimetallabicyclic products $Cp_2M(\mu\text{-}\eta^1:\eta^2\text{-}RCCR)(\mu\text{-}X)[M^2]$ which contain a planar-tetracoordinate carbon center in the $\mu$-$\eta^1:\eta^2$-hydrocarbyl bridge. Thus, ($\eta^2$-cyclohexyne)($PMe_3$)$ZrCp_2$ (**4a**) reacts in this way with excess trimethylgallium to give $Cp_2Zr(\mu\text{-}\eta^1:\eta^2\text{-}C_6H_8)(\mu\text{-}CH_3)GaMe_2$ (**6a**). Complex **6a** is one of the rare examples of a gallium compound containing σ-hydrocarbyl bridges to this heavy main group metal. Complex **6a** was characterized by X-ray diffraction. It crystallizes in space group $P2_1/c$ with cell parameters $a$ = 9.007 (3) Å, $b$ = 8.195 (2) Å, $c$ = 25.404 (4) Å, $\beta$ = 91.30 (1)°, $Z$ = 4, $R$ = 0.056, and $R_w$ = 0.066. Complex **6a** contains a planar-tetracoordinate carbon atom C(2) with pertinent bond distances and angles of 2.423 (5) Å [Zr–C(2)], 2.096 (5) Å [Ga–C(2)], 1.572 (8) Å [C(2)–C(3)], 1.314 (7) Å [C(1)–C(2)], 119.5 (4)° [C(3)–C(2)–C(1)], 100.3 (3)° [C(3)–C(2)–Ga], 79.3 (1)° [Ga–C(2)–Zr], and 61.1 (3)° [C(1)–C(2)–Zr]. Both Cp rings are disordered. Zirconium and gallium seem to form a three-center two-electron bond with C(2). The planar-tetracoordinate geometry at carbon atom C(2) is probably electronically stabilized by the σ-donor properties of the attached metal centers and by a π-conjugative interaction of the C(2)–C(1)–Zr moiety normal to the σ-plane. ($\eta^2$-1,2-Didehydrobenzene)($PMe_3$)$ZrCp_2$ (**4b**) reacts analogously with trimethylgallium to give $Cp_2Zr(\mu\text{-}\eta^1:\eta^2\text{-}C_6H_4)(\mu\text{-}CH_3)GaMe_2$ (**6b**) in almost quantitative yield. Complex **6b** crystallizes isomorphously to the corresponding Al compound in space group $P2_1/n$ with cell parameters $a$ = 9.126 (1) Å, $b$ = 14.080 (2) Å, $c$ = 14.323 (1) Å, $\beta$ = 103.88 (1)°, $Z$ = 4, $R$ = 0.062, and $R_w$ = 0.038. It also contains a planar-tetracoordinate carbon atom [C(2)]. The reaction of Ph—C≡C—$GaMe_2$ (**7**) with (hydrido)zirconocene chloride produces $Cp_2Zr(\mu\text{-}PhCCH)(\mu\text{-}Cl)GaMe_2$ (**9**) which is probably also a similarly structured "anti-van't Hoff/LeBel complex". Complexes **6a** and **6b** react with ethylene or norbornene at room temperature with liberation of $Me_3Ga$ and formation of five-membered metallacyclic products (e.g., bis($\eta$-cyclopentadienyl)zirconaindane is obtained from **6b** and ethylene).

Dimetallic complexes containing the main group metal gallium combined with a variety of d-block elements are rather abundant although it is noticeable that they always seem to contain metal–metal bonds and apparently never $\mu$-hydrocarbyl bridges to connect the metal centers.[1] In this respect the group 3 element gallium seems to behave strikingly different from its lighter homologue aluminum from which numerous examples of σ-hydrocarbyl-bridged complexes are known.[2] The observed structural differences of the respective homoleptic $R_3M$ species may serve to illustrate this point: trimethylgallium has shown to be a monomer in solution as well as in the gas-phase,[3] whereas the $Me_2Al(\mu\text{-}CH_3)_2AlMe_2$ trimethylaluminum dimer is favored by some 20 kcal mol$^{-1}$ over its dissociated monometallic building blocks.[4] Gallium even seems to disfavour π-bridging to some extent. In contrast to the strong Al–C(Ar) linkages in the stable ($R_2Al\text{-}C_6H_5$) dimers,[5] the aryl–carbon to gallium π-interaction in, e.g., (phenyl)$_3$Ga associates in the solid state seems to be rather weak.[6,7]

We have recently found an unprecedentedly simple way of synthesizing heterodimetallic hydrocarbyl-bridged zirconium (or hafnium)/aluminum compounds (**3**) that contain a planar-tetracoordinate carbon in the bridge. The essential step of the reaction sequence consists of the addition of the main group metal component X-[$M^2$] (**2**) to a very reactive ($\eta^2$-alkyne)transition metal reagent (**1**) which is usually generated in situ from an appropriate precursor in the course of the reaction.[8]

Scheme I



 (1)

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† Organisch-Chemisches Institut der Universität Münster.
‡ Max-Planck-Institut für Kohlenforschung.

(1) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990**, *31*, 91. Fischer, R. A.; Behm, J. *Chem. Ber.* **1992**, *125*, 37.

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The bridgehead carbon center of the dimetallabicyclic framework of the complexes **3** is planar-tetracoordinate. This unusual coordination geometry of tetravalent carbon has rarely been observed previously in stable and isolable compounds.[9] It has been due to the simple synthetic entry depicted above that many such "anti-van't Hoff/LeBel complexes" were prepared and isolated just recently.[8]

Planar-tetracoordinate carbon (**A**) contains an electron deficient $\sigma$-system (six electrons making four bonds) and an occupied p-orbital.[10] In the thermodynamically stable planar-tetracoordinate carbon compounds **3** the $\sigma$-donor properties of the two metals attached to carbon atom C(2) probably serve to stabilize the $\sigma$-system by forming a stable three-center two-electron bond. In addition, there seems to be a substantial $\pi$-conjugative C(2)–C(1)–M$^1$ interaction normal to the $\sigma$-plane that very much helps to make the "unnatural" planar-tetracoordinate bonding geometry of the bridging carbon atom C(2) thermodynamically favorable. Complexes **3a–c** are typical examples of this type of compounds that were just recently prepared and described. The resonance forms **B** and **C** may possibly serve to describe some of the major factors leading to the remarkable electronic stabilization of the planar-tetracoordinate carbon center in these dimetallic complexes.

We have now carried out a variety of reactions according to the general synthetic scheme depicted in eq 1 that have led to doubly $\sigma$-hydrocarbyl bridged gallium/zirconium compounds. The obtained reaction products are quite remarkable with regard to two rather uncommon structural features: the obtained thermodynamically stable complexes contain planar-tetracoordinate carbon, electronically stabilized by the combined action of the alkylgallium moiety and the bent metallocene unit, and they exhibit a $R_2Ga(\mu\text{-}R^1,\mu\text{-}R^2)$ unit in which the gallium center is connected to the adjacent early transition metal center by forming two stable $\sigma$-hydrocarbyl bridges.[7] Two representative examples of these unusually structured $R_2Ga(\mu\text{-}R^1,\mu\text{-}R^2)ZrCp_2$ complexes will be described in this article and discussed with regard to their structural properties.

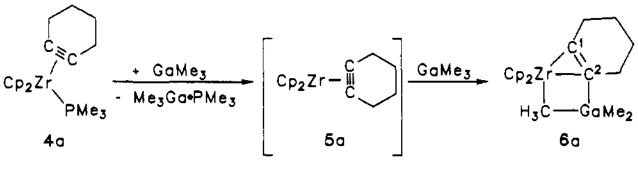
## Results and Discussion

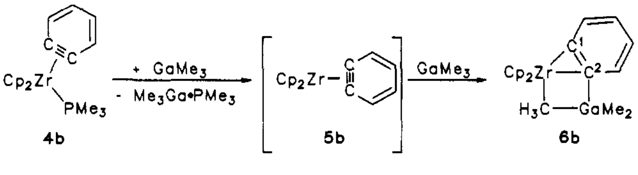
**Preparation of the $\sigma$-Hydrocarbyl-Bridged Gallium/Zirconium Complexes.** We used S. L. Buchwald's ($\eta^2$-cyclohexyne)($PMe_3$)zirconocene (**4a**)[11] as a starting material of our synthesis. Trimethylgallium was employed as a Lewis acid to abstract the Lewis basic trimethylphosphane ligand from **4** and to serve subsequently as a coupling component to react with the in situ generated reactive ($\eta^2$-cyclohexyne)$ZrCp_2$ intermediate (**5a**). We have thus reacted **4** with a 4-fold molar excess of $Me_3Ga$. The formed $Me_3Ga{\cdot}PMe_3$ adduct was removed along with the solvent and some unused trimethylgallium in vacuo to give the dimetallabicyclic ($\eta^2$-cyclohexyne)$ZrCp_2/Me_3Ga$ addition product (**6a**) in almost quantitative yield.

Complex **6a** exhibits characteristic $^1H$ NMR resonances (in benzene-$d_6$) at $\delta$ 5.28 (Cp), –0.22 [Zr]($\mu$-$CH_3$)[Ga], and –0.02 (terminal $(H_3C)_2$[Ga]) and $^{13}C$ NMR signals (in benzene-$d_6$) at $\delta$ 108.7 (Cp), –3.1 ($GaMe_2$), and –17.2 ($\mu$-$CH_3$). The sp$^2$-hybridized carbon atoms of the bridging [Zr]($\mu$-$\eta^1$:$\eta^2$-alkyne)[Ga] ligand appear at $\delta$ 197.3 (Zr—C≡) and $\delta$ 109.3; the latter signal is attributed to the planar-tetracoordinate carbon center [C(2)]. Very similar chemical shift values were observed for the Zr/Al "anti-van't Hoff/LeBel complexes" **3b** [$\delta$ C(1), 207.6; $\delta$ C(2), 108.9] and $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-cyclohexyne})(\mu\text{-}CH_3)AlMe_2$ [**3d**; $\delta$ C(1), 207.5; $\delta$ C(2), 110.3; $\mu$-$CH_3$, $\delta$ –17.0, $^1J_{CH}$ = 114 Hz; $AlMe_2$, –6.7, $^1J_{CH}$ = 112 Hz].[8]

($\eta^2$-1,2-Didehydrobenzene)($PMe_3$)$ZrCp_2$ (**4b**)[12] is another easily available starting material for our synthesis. The reaction of **4b** with excess trimethylgallium cleanly gives a near to quantitative yield of the $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_3)GaMe_2$ complex (**6b**). Again, $Me_3Ga$ very nicely serves as a dual purpose reagent, namely to remove $PMe_3$ from the phosphane-stabilized (aryne)metallocene and then to trap the thus generated very reactive ($\eta^2$-1,2-didehydrobenzene)metallocene intermediate (**5b**)[13] with formation of the stable dimetallabicyclic system **6b**.

The $^{13}C$ NMR resonance of the planar-tetracoordinate carbon atom [C(2)] of **6b** is observed at $\delta$ 117.3. This compares to C(2) resonances at $\delta$ 116.1 of the analogous zirconium/aluminum complex **3b** and $\delta$ 114.9 of $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-1,2-didehydrobenzene})(\mu\text{-}H)Al(iBu)_2$ (**3e**).[8] As expected the C(1) $^{13}C$ NMR resonance of the $\mu$-$\eta^1$:$\eta^2$-aryne bridge of complex **6b** is at much higher $\delta$-values [$\delta$ 187.3 in benzene-$d_6$; this is only slightly less shifted as compared to the Zr,Al($\mu$-$\eta^1$:$\eta^2$-aryne) compounds **3b** ($\delta$ 193.9) and **3e** ($\delta$ 193.4)[8]]. The $^1H/^{13}C$ NMR methyl resonances of the $GaMe_2$ unit of **6b** are at $\delta$ 0.11 (s, 6 H) and $\delta$ –1.4 ($^1J_{CH}$ = 120 Hz). The $\mu$-$CH_3$ signals are observed at $\delta$ –0.21 ($^1H$) and $\delta$ –14.5 ($^1J_{CH}$ = 121 Hz), respectively. The respective $^1H/^{13}C$ NMR ($\mu$-$CH_3$)$AlMe_2$ resonances of the analogous Zr/Al complex were found to have very similar shift values [**3c**: $\delta$ –0.10 ($^1H$), –4.7 ($^{13}C$)($\mu$-$CH_3$); $\delta$ –0.23 ($^1H$), –14.9 ($^{13}C$) ($AlMe_2$)].





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(2) Wells, A. F. *Structural Inorganic Chemistry*; Clarendon Press: Oxford, 1984; pp 978–981. Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, 1982; Vol. 1, pp 1–42, pp 555–724.

(3) Beagley, B.; Schmidling, D. G.; Steer, I. A. *J. Mol. Struct.* **1974**, *21*, 437. See, also: Muller, N.; Otermat, A. L. *Inorg. Chem.* **1965**, *4*, 296. Hartmann, H.; Lutsche, H. *Naturwissenschaften* **1961**, *48*, 601. Beachley, O. T., Jr.; Simmons, R. G. *Inorg. Chem.* **1980**, *19*, 1021.

(4) Laubengayer, A. W.; Gilliam, W. F. *J. Am. Chem. Soc.* **1941**, *63*, 477. Huffman, J. C.; Streib, W. E. *J. Chem. Soc., Chem. Commun.* **1971**, 911.

(5) Malone, J. F.; McDonald, W. S. *J. Chem. Soc., Dalton Trans.* **1972**, 2646, 2649.

(6) Malone, J. F.; McDonald, W. S. *J. Chem. Soc. A* **1970**, 3362.

(7) For a rare example where gallium forms $\sigma$-hydrocarbyl bridges to another metal see, e.g.: Uhl, W.; Klinkhammer, K.-W.; Layh, M.; Massa, W. *Chem. Ber.* **1991**, *124*, 279. See, also: Lee, B.; Pennington, W. T.; Laske, J. A.; Robinson, G. H. *Organometallics* **1990**, *9*, 2864.

(8) Erker, G.; Zwettler, R.; Krüger, C.; Noe, R.; Werner, S. *J. Am. Chem. Soc.* **1990**, *112*, 9620. Erker, G.; Albrecht, M.; Krüger, C.; Werner, S. *Organometallics* **1991**, *10*, 3791. Albrecht, M.; Erker, G.; Nolte, M.; Krüger, C. *J. Organomet. Chem.* **1992**, *427*, C21. Erker, G. *Comments Inorg. Chem.* **1992**, *13*, 111. Erker, G.; Albrecht, M.; Werner, S.; Nolte, M.; Krüger, C. *Chem. Ber.* **1992**, *125*, 1953. Erker, G.; Albrecht, M.; Krüger, C.; Werner, S.; Binger, P.; Langhauser, F. *Organometallics*, in press.

(9) Cayton, R. H.; Chacon, S. T.; Chisholm, M. H.; Hampden-Smith, M. J.; Huffmann, J. C.; Folting, K.; Ellis, P. D.; Huggins, B. A. *Angew. Chem.* **1989**, *101*, 1547. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1523. Chacon, S. T.; Chisholm, M. H.; Folting, K.; Huffmann, J. C.; Hampden-Smith, M. J. *Organometallics* **1991**, *10*, 3722. Beringhelli, T.; Ciani, G.; D'Alfonso, G.; Sironi, A.; Freni, M. *J. Chem. Soc., Chem. Commun.* **1985**, 978. Cotton, F. A.; Millar, M. J. *J. Am. Chem. Soc.* **1977**, *99*, 7886. Harder, S.; Boersma, J.; Brandsma, L.; van Heteren, A.; Kanters, J. A.; Bauer, W.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1988**, *110*, 7802. Buchwald, S. L.; Lucas, E. A.; Davies, W. M. *J. Am. Chem. Soc.* **1989**, *111*, 397. See, also: Uhl, W.; Layh, M.; Massa, W. *Chem. Ber.* **1991**, *124*, 1511. Layh, M.; Uhl, W. *Polyhedron* **1990**, *9*, 277. Keese, R.; Pfenniger, A.; Roesle, A. *Helv. Chim. Acta* **1979**, *62*, 326. Keese, R. *Nachr. Chem. Techn. Lab.* **1982**, *30*, 844. Krohn, K. *Nachr. Chem. Techn. Lab.* **1987**, *35*, 264.

(10) Hoffmann, R.; Alder, R. W.; Wilcox, C. F., Jr. *J. Am. Chem. Soc.* **1970**, *92*, 4992. Hoffmann, R. *Pure Appl. Chem.* **1971**, *28*, 181. Collins, J. B.; Dill, J. C.; Jemmis, E. D.; Apeloig, Y.; Schleyer, P. v. R.; Seeger, R.; Pople, A. *J. Am. Chem. Soc.* **1976**, *98*, 5419, and references cited therein.

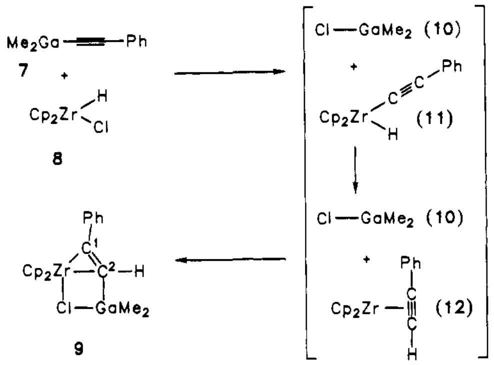
(11) Buchwald, S. L.; Lum, R. T.; Dewan, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7441.

(12) Buchwald, S. L.; Watson, B. T.; Huffman, J. C. *J. Am. Chem. Soc.* **1986**, *108*, 7411.

(13) Erker, G.; Kropp, K. *J. Am. Chem. Soc.* **1979**, *101*, 3659. Reviews: Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047. Bennett, M. A.; Schwemlein, H. P. *Angew. Chem.* **1989**, *101*, 1349; *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1296.

The reaction of $Cp_2Zr(H)Cl$ with Ph—C≡C—$GaMe_2$ gives a single reaction product, isolated in 68% yield, of the composition $Cp_2Zr(\mu\text{-}PhCCH)(\mu\text{-}Cl)GaMe_2$ (**9**). This complex is probably analogous to the dimetallabicyclic Zr/Ga compounds **6a** and **6b** described above, although in this case the definitive structural proof by X-ray crystallography is still lacking. Therefore, in contrast to the planar-tetracoordinate carbon compounds **6a** and **6b**, whose structures were determined by X-ray diffraction analyses (see below), the analogous structural assignment of **9** as another example of an "anti van't Hoff/LeBel complex" is only tentative and must at present be of some speculative nature.

The methine carbon resonance in **9** is at $\delta$ 146.8 and has a $^1J_{CH}$ coupling constant of 154 Hz. The signal of the adjacent quaternary carbon center [C(1)] of the $\mu$-PhCCH bridging ligand is found at $\delta$ 258.9. There are a few related complexes known to be formed in the reaction of $Cp_2Zr(H)Cl$ and Ph—C≡C—$AlMe_2$ or Me—C≡C—$AlMe_2$, respectively. These also seem to contain the $[Zr](\mu\text{-}\eta^1\text{:}\eta^2\text{-}RC^1C^2H)[M^2]$ (**13a** R = Ph, **13b** R = $CH_3$; $[M^2]$ = $AlMe_2$) building block with carbon atom C(2) probably being planar-tetracoordinate. The respective $^{13}C$ NMR resonances are found at $\delta$ 282.9, 147.2 ($^1J_{CH}$ = 150 Hz, **13a**) and $\delta$ 198.8, 142.1 ($^1J_{CH}$ = 150 Hz, **13b**).[8]



The reaction sequence leading to **9** is probably initiated by a σ-ligand metathesis between the alkynylgallium reagent (**7**) and (hydrido)zirconocene chloride (**8**) (and not by a simple hydrozirconation reaction).[14] The (hydrido)(alkynyl)$ZrCp_2$ species formed seems to be unstable under the reaction conditions applied and may undergo reductive elimination. The resulting reactive ($\eta^2$-alkyne)zirconocene intermediate then adds the $ClGaMe_2$ reagent formed in the initiating step to give the thermodynamically favored dimetallabicyclic product **9**. The overall reaction sequence is thus potentially just another example of our novel synthetic pathway to this general type of planar-tetracoordinate carbon complexes as depicted in eq 1 (see above).[8]

**X-ray Crystal Structure Analyses of the Dimetallic μ-(σ-Hydrocarbyl)gallium/Zirconium Complexes 6a and 6b.** Crystals of complex **6a** suited for the X-ray crystal structure determination were obtained upon cooling a pentane solution of $Cp_2Zr(\mu\text{-}\eta^1\text{:}\eta^2\text{-}C_6H_8)(\mu\text{-}CH_3)GaMe_2$ to −30 °C. In the solid state **6a** contains a bent metallocene unit with a maximum σ-ligand angle [C(1)–Zr–C(9)] of 123.6 (2)°. Both Cp rings are disordered; the disorder effects have been included in the refinement with 50% occupancy of the corresponding atoms. Accordingly, no hydrogen atoms were located at these centers. The Zr–C(Cp) distances are in a narrow range between 2.49 (2) and 2.59 (2) Å.[15]

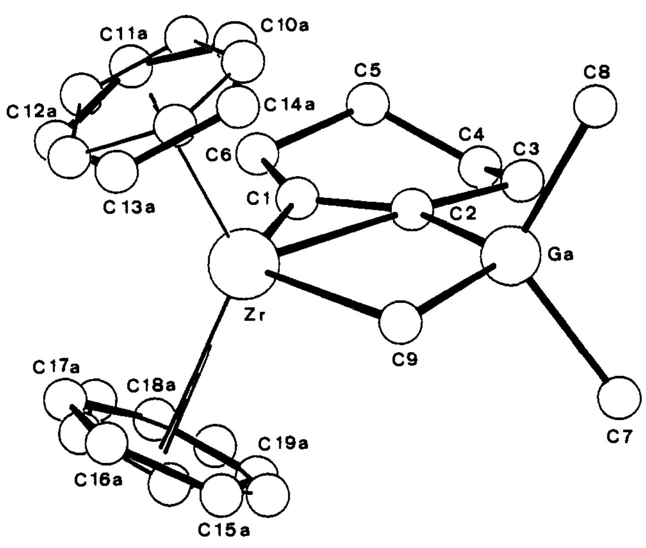


Figure 1. A view of the molecular geometry of complex **6a**; carbon atom C(2) is planar-tetracoordinate.

Table I. Selected Bond Lengths (Å) and Angles (deg) of **6a**

| | | | |
|---|---|---|---|
| Zr–C(1) | 2.126 (5) | Zr–C(2) | 2.423 (5) |
| Zr–C(9) | 2.597 (6) | Ga–C(2) | 2.096 (5) |
| Ga–C(7) | 1.968 (7) | Ga–C(8) | 1.979 (7) |
| Ga–C(9) | 2.142 (7) | C(1)–C(2) | 1.314 (7) |
| C(1)–C(6) | 1.508 (7) | C(2)–C(3) | 1.572 (8) |
| C(3)–C(4) | 1.49 (1) | C(4)–C(5) | 1.41 (1) |
| C(5)–C(6) | 1.558 (9) | | |
| | | | |
| C(9)–Zr–C(2) | 90.9 (2) | C(9)–Zr–C(1) | 123.6 (2) |
| C(2)–Zr–C(1) | 32.8 (2) | C(9)–Ga–C(8) | 107.3 (3) |
| C(9)–Ga–C(7) | 101.4 (3) | C(9)–Ga–C(2) | 115.2 (2) |
| C(8)–Ga–C(7) | 116.2 (3) | C(8)–Ga–C(2) | 106.9 (2) |
| C(7)–Ga–C(2) | 110.1 (2) | C(6)–C(1)–C(2) | 126.4 (4) |
| C(6)–C(1)–Zr | 147.4 (4) | C(2)–C(1)–Zr | 86.2 (3) |
| C(3)–C(2)–C(1) | 119.5 (4) | C(3)–C(2)–Ga | 100.3 (3) |
| C(3)–C(2)–Zr | 177.2 (4) | C(1)–C(2)–Ga | 140.2 (4) |
| C(1)–C(2)–Zr | 61.1 (3) | Ga–C(2)–Zr | 79.3 (1) |
| C(4)–C(3)–C(2) | 112.2 (5) | C(5)–C(4)–C(3) | 117.9 (8) |
| C(6)–C(5)–C(4) | 113.3 (6) | C(5)–C(6)–C(1) | 112.0 (5) |
| Ga–C(9)–Zr | 74.6 (2) | | |

The most remarkable structural feature of **6a** is that the gallium center is connected to zirconium by means of two different σ-hydrocarbyl bridges. One of them contains the cyclo-$C_6H_8$ system, which is $\eta^1$-bonded to gallium and $\eta^2$-coordinated to zirconium. It is noteworthy that carbon atom C(2) is planar-tetracoordinate. It is connected to four neighboring atoms in the σ-plane, namely to carbon atoms C(1) and C(3) and to both metal centers.

The C(2)–C(3) distance is 1.572 (8) Å, whereas the C(2)–C(1) bond is much shorter at 1.314 (7) Å which is within the range of a C($sp^2$)–C($sp^2$) carbon–carbon double bond.[16] The Zr–C(2) bond length is 2.423 (5) Å. This is slightly longer than expected for an ordinary $Cp_2Zr$–C($sp^2$) single bond[17] but still shorter than the average Zr–C(Cp) separation (see above). The C(2)–Ga distance is at 2.096 (5) Å also slightly longer than usually observed for gallium–carbon σ-bonds (trimethylgallium has a Ga–C($sp^3$) bond length of 1.967 (2) Å;[3] this compares nicely with the Ga–C(7) and Ga–C(8) distances found in **6a** at 1.968 (7) and 1.979 (7) Å, respectively). The bonding geometry at C(2) is as expected for a typical example of an electronically stabilized planar-tetracoordinate carbon derivative, exhibiting a three-center two-electron metal–carbon–metal σ-interaction (the corresponding bonding angles of the coplanar σ-coordination at C(2) are 119.5 (4)° [C(1)–C(2)–C(3)], 100.3 (3)° [C(3)–C(2)–Ga], 79.3 (1)° [Ga–C(2)–Zr], and 61.1 (3)° [Zr–C(2)–C(1)]).

The planar-tetracoordinate bonding situation at the carbon atom C(2) is probably further stabilized by a π-conjugative interaction taking place normal to the σ-ligand plane and involving the C-

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(14) For related pathways taken in "anomalous" hydrozirconation reactions, see: Hyla-Kryspin, I.; Gleiter, R.; Krüger, C.; Zwettler, R.; Erker, G. *Organometallics* **1990**, *9*, 517, 524. Erker, G.; Zwettler, R. *J. Organomet. Chem.* **1991**, *409*, 179. See also: Erker, G.; Schlund, R.; Krüger, C. *Organometallics* **1989**, *8*, 2349.

(15) For a comparison with typical examples of other $d^0$-configurated early transition metal bent metallocene complexes see, e.g.: Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729. Cardin, D. J.; Lappert, M. F.; Raston, C. L. *Chemistry of Organo-Zirconium and -Hafnium Compounds*; Wiley: New York, 1986; and references cited therein.

(16) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. II* **1987**, S1.

(17) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1.

**Table II.** Selected Bond Lengths (Å) and Angles (deg) of **6b**

| | | | |
|---|---|---|---|
| Zr–C(1) | 2.174 (7) | Zr–C(2) | 2.509 (7) |
| Zr–C(9) | 2.591 (7) | Ga–C(2) | 2.091 (7) |
| Ga–C(7) | 1.992 (8) | Ga–C(8) | 1.958 (9) |
| Ga–C(9) | 2.169 (7) | C(1)–C(2) | 1.37 (1) |
| C(1)–C(6) | 1.40 (1) | C(2)–C(3) | 1.41 (1) |
| C(3)–C(4) | 1.34 (1) | C(4)–C(5) | 1.37 (1) |
| C(5)–C(6) | 1.37 (1) | | |
| C(9)–Zr–C(2) | 90.1 (2) | C(9)–Zr–C(1) | 123.1 (2) |
| C(2)–Zr–C(1) | 33.0 (2) | C(9)–Ga–C(8) | 103.7 (3) |
| C(9)–Ga–C(7) | 105.0 (3) | C(9)–Ga–C(2) | 115.8 (3) |
| C(8)–Ga–C(7) | 117.8 (4) | C(8)–Ga–C(2) | 106.0 (3) |
| C(7)–Ga–C(2) | 108.8 (3) | C(6)–C(1)–C(2) | 121.4 (7) |
| C(6)–C(1)–Zr | 151.5 (6) | C(2)–C(1)–Zr | 87.1 (4) |
| C(3)–C(2)–C(1) | 117.4 (6) | C(3)–C(2)–Ga | 104.1 (5) |
| C(3)–C(2)–Zr | 177.3 (5) | C(1)–C(2)–Ga | 138.5 (5) |
| C(1)–C(2)–Zr | 59.9 (4) | Ga–C(2)–Zr | 78.6 (2) |
| C(4)–C(3)–C(2) | 121.2 (7) | C(5)–C(4)–C(3) | 121.2 (8) |
| C(6)–C(5)–C(4) | 119.6 (8) | C(5)–C(6)–C(1) | 119.1 (7) |
| Ga–C(9)–Zr | 75.4 (2) | | |

(2)–C(1)–Zr moiety as indicated by the observed extremely short Zr–C(1) distance of 2.126 (5) Å. This is one of the shortest $Cp_2Zr$–C bond lengths ever observed. It is even markedly shorter than the Zr–C(sp) bond length in $Cp_2Zr(CO)_2$ (2.18 Å).[18,19]

The gallium atom in the heterodimetallic complex **6a** is tetracoordinate. It features a pseudotetrahedral bonding geometry with two $\sigma$-bridging groups connecting it with zirconium. One bridge is made of the $\mu$-$\eta^1$:$\eta^2$-$C_6H_8$ group involving an $sp^2$-orbital at C(2) in a three-center two-electron bonding situation as described above. The Ga and Zr atoms (Ga···Zr separation: 2.893 (1) Å) are further connected by means of a $\mu$-$CH_3$ group. The Zr–C(9)–Ga angle at the bridging methyl carbon (which is probably $sp^3$-hybridized) is 74.6 (2)°. The Zr–C(9) bond length is rather long at 2.597 (6) Å, and so is the Ga–C(9) bond at 2.142 (7). The C(9)–Ga–C(2) angle is slightly larger than expected for tetrahedral [115.2 (2)°]. For steric reasons the C(7)–Ga–C(8) angle is also slightly widened at 116.2 (3)°, whereas the remaining bonding angles at gallium are all somewhat smaller [C(7)–Ga–C(2), 110.1 (2)°; C(8)–Ga–C(2), 106.9 (2)°; C(9)–Ga–C(7), 101.4 (3)°; C(9)–Ga–C(8), 107.3 (3)°]. Complex **6a** thus is an example of a stable heterodimetallic gallium/zirconium compound where the heavy main group metal forms two reasonably stable $\sigma$-hydrocarbyl bridges connecting it with the electrophilic early transition metal center.[7]

Complex **6b** is isomorphous to the analogous $Cp_2Zr(\mu$-$\eta^1$:$\eta^2$-$C_6H_4)(\mu$-$CH_3)AlMe_2$ complex **3c**.[8] The methyl bridge between Zr and Ga (Zr···Ga separation: 2.930 (1) Å) is only loosely bound to the transition metal ($d$ = Zr-C(9) 2.591 (7) Å). The Ga–C(9) distance [2.169 (7) Å] is longer than the Ga–C bond lengths of the terminal gallium methyl groups [$d$ = Ga–C(7) 1.992 (8); Ga–C(8) 1.958 (9) Å]. The bond angles around gallium in complex **6b** are similar to those observed in **6a** (see Table II).

Complex **6b** contains a planar-tetracoordinate carbon atom [C(2)] that is part of the $\mu$-$\eta^1$:$\eta^2$-1,2-didehydrobenzene $\sigma$-hydrocarbyl bridge. The four $\sigma$-bonds around C(2) are oriented perfectly coplanar. The respective bond lengths are 2.509 (7) Å [C(2)–Zr], 2.091 (7) Å [C(2)–Ga], 1.41 (1) Å [C(2)–C(3)], and 1.37 (1) Å [C(2)–C(1)]. The bond angles of the $\sigma$-system centered at C(2) are as follows: 117.4 (6)° [C(3)–C(2)–C(1)], 104.1 (5)° [C(3)–C(2)–Ga], 78.6 (2)° [Ga–C(2)–Zr], and 59.9 (4)° [C(1)–C(2)–Zr]. Similar to **6a**, the Zr–C(1) bond in **6b** is very short at 2.174 (7) Å [angle Zr–C(1)–C(2), 87.1 (4)°]. This could be interpreted as arising from a $\pi$-conjugative interaction between C(2), C(1), and zirconium which is removing p-electron density from C(2) which increases the electronic stabilization of the planar-tetracoordinate bonding situation at this carbon atom.

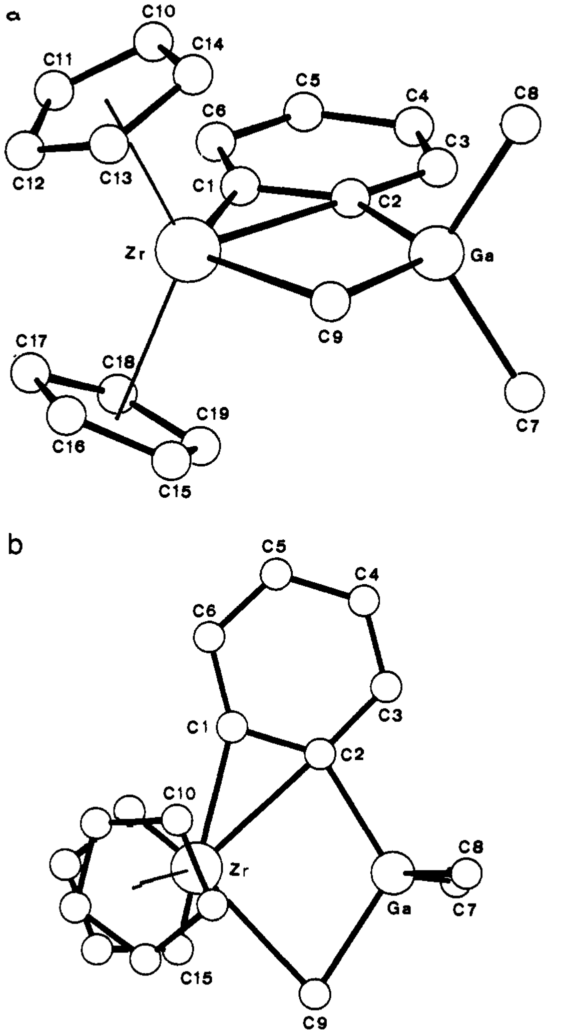

**Figure 2.** Two projections of the molecular structure of the heterodimetallic complex **6b**; carbon atom C(2) is planar-tetracoordinate.

**Exchange Reactions of Complexes 6a and 6b.** From the X-ray crystal structure analyses it appears that trimethylgallium is rather loosely bound to the ($\eta^2$-aryne)- and ($\eta^2$-cyclohexyne)metallocene building blocks in the dimetallabicyclic complexes **6a** and **6b**, respectively. Therefore, it was tempting to investigate whether it was possible to reverse the reaction as depicted in eq 1 (see above) using these specific examples to carry out thermally induced exchange reactions. We have performed a couple of preliminary orientating experiments that have indeed revealed that the $Me_3Ga$ unit can be removed from the complexes **6a** and **6b** and replaced by organic building blocks.

The complex $Cp_2Zr(\mu$-$\eta^1$:$\eta^2$-$C_6H_8)(\mu$-$CH_3)GaMe_2$ (**6a**) reacts readily at room temperature with norbornene to give trimethylgallium and the metallacyclic reaction product **13**. The norbornene/($\eta^2$-cyclohexyne)$ZrCp_2$ addition product was tentatively identified spectroscopically. Its NMR spectra relate very characteristically to those of the long known very similarly structured five-membered metallacycle obtained by means of ($\eta^2$-aryne)-zirconocene/norbornene cycloaddition.[13]

Complex **6b** reacts analogously with ethylene. At ambient temperature trimethylgallium is rapidly liberated. At the same time the remaining ($\eta^2$-aryne)zirconocene fragment takes up 1 equiv of ethylene to form the metallaindane system **14**. The identification of **14** was carried out by a comparison with an authentic sample.[13] Prolonged treatment of the reaction mixture

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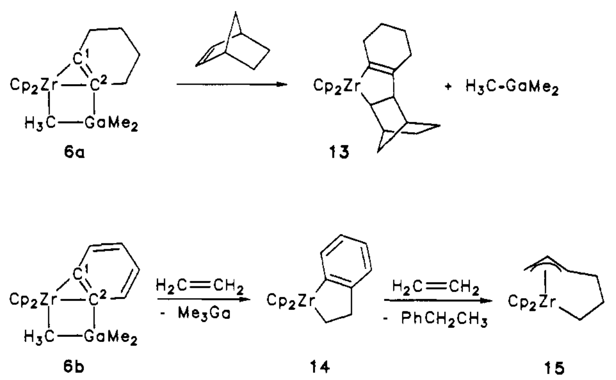
(18) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812. Sikora, D. J.; Rausch, M.-D.; Rogers, R. D.; Atwood, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 1265. See, also: Erker, G.; Czisch, P.; Mynott, R.; Tsay, Y.-H.; Krüger, C. *Organometallics* **1985**, *4*, 1310. Erker, G.; Frömberg, W.; Mynott, R.; Gabor, B.; Krüger, C. *Angew. Chem.* **1986**, *98*, 456. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 463.

(19) The partial carbene complex character of the Zr–C(2) linkage is further supported by the observed $^{13}C$ NMR chemical shifts of the complexes 3. See for a comparison: Hartner, F. W., Jr.; Schwartz, J.; Clift, S. M. *J. Am. Chem. Soc.* **1983**, *105*, 640. Clift, S. M.; Schwartz, J. *J. Am. Chem. Soc.* **1984**, *106*, 8300.



with ethylene (36 h at room temperature) eventually led to the formation of **15**[20] which is known to be a product of a subsequent reaction of the metallaindane **14** with this specific olefin.[13]

## Conclusions

Alkyl-bridged gallium compounds are very rare. In this respect this heavy group 3 metal behaves quite differently from the analogous aluminum compounds. Complexes **6** represent noteworthy exceptions of this often observed difference in coordination behavior. It appears that here the heterodimetallic Zr,Ga complexes **6** behave structurally similar to their respective Zr,Al analogues (e.g., **3c**,**d**).[8] In these compounds the tendency of forming a stable planar-tetracoordinate geometry at the carbon atom C(2) of the $\mu$-$\eta^1$:$\eta^2$-RCCR′ type bridging σ-hydrocarbyl ligand within the dimetallabicyclic framework seems to be so pronounced that it even helps to overcome the often observed reluctance of the element gallium to form σ-hydrocarbyl bridges.[2,3] The dimetallabicyclo[2.1.0]pentane derived framework of the complexes **3** and **6** seems to be ideally suited to allow the contained metal centers to electronically stabilize the uncommon planar-tetracoordinate geometry of carbon.[10] In this arrangement both metal centers can easily form a three-center two-electron bond in the σ-ligand plane without any steric constraints. In fact, the [M$^1$] and [M$^2$] building blocks (Zr and Al in **3**; Zr and Ga in **6**) seem to become very favorably geometrically arranged for this type of bonding by means of the single centered $\mu$-X ligand bridging between them. This energetically overall favorable situation may be the reason why even gallium easily forms such a bridge in these complexes. In addition, the planar dimetallabicyclic σ-framework allows for the formation of a substantial π-conjugative interaction of the C(2)–C(1)–Zr moiety which probably greatly helps to stabilize the unnatural planar-tetracoordinate geometry of carbon to such an extent. Our study shows that thermodynamically very stable "anti-van't Hoff/LeBel compounds"[8] can easily be prepared and isolated in high yield if the overall composition allows for a suitable electronic stabilization by means of attached or incorporated σ-donor/π-acceptor substituents. It is likely that variants of our synthetic pathway will allow for the preparation for many more examples of stable compounds containing planar-tetracoordinate carbon. Investigations aimed at learning about special chemical properties associated with the unusual structural features of "anti-van't Hoff/LeBel complexes" are currently carried out in our laboratory.

## Experimental Section

All reactions were carried out in an inert atmosphere (argon) using Schlenk-type glassware or a drybox. The following instruments were used for product characterization: Bruker AC 200 P NMR spectrometer ($^1$H, 200 MHz; $^{13}$C, 50 MHz), Nicolet 5 DXC FT IR spectrometer, Gallenkamp melting point apparatus (samples sealed in capillaries under argon; melting points uncorrected); elemental analyses: Foss-Heraeus CHN-Rapid; and differential scanning calorimetry: DuPont DSC, STA Instruments. All solvents were dried and distilled under argon prior to use. The starting materials ($\eta^2$-cyclohexyne)(PMe$_3$)ZrCp$_2$ (**4a**),[11] ($\eta^2$-1,2-didehydrobenzene)(PMe$_3$)ZrCp$_2$ (**4b**), Ph—C≡C—GaMe$_2$ (**7**),[21] and the oligomeric [Cp$_2$Zr(H)Cl]$_x$ (**8**)[14] were prepared according to literature procedures.

Table III. Details of the X-ray Diffraction Data Collection and Structure Solution of **6a**[a] and **6b**[b]

| | **6a** | **6b** |
|---|---|---|
| formula | $C_{19}H_{27}GaZr$ | $C_{19}H_{23}GaZr$ |
| mol wt | 416.4 | 412.3 |
| crystal color | white | white |
| crystal system | monoclinic | monoclinic |
| space group [no.] | $P2_1/c$ [14] | $P2_1/n$ [14] |
| $a$, Å | 9.007 (3) | 9.126 (1) |
| $b$, Å | 8.195 (2) | 14.080 (2) |
| $c$, Å | 25.404 (4) | 14.323 (1) |
| $\beta$, deg | 91.30 (1) | 103.88 (1) |
| $V$, Å$^3$ | 1874.5 | 1786.6 |
| $Z$ | 4 | 4 |
| $D_{calcd}$, g cm$^{-3}$ | 1.48 | 1.53 |
| $\mu$, cm$^{-1}$ | 19.73 | 20.69 |
| Mo K$\alpha$ radiation, $\lambda$, Å | 0.71069 | 0.71069 |
| $F$(000), e | 848 | 832 |
| diffractometer | Enraf-Nonius CAD4 | |
| scan mode | $\omega$–2$\theta$ | $\omega$–2$\theta$ |
| $[(\sin\theta)/\lambda]_{max}$, Å$^{-1}$ | 0.70 | 0.65 |
| $T$, °C | 20 | 20 |
| abs correction (min–max) | analytical<br>1.441–1.761 | empirical<br>0.826–0.999 |
| no. of measd reflcns ($\pm h$,$+k$,$+l$) | 5988 | 4408 |
| no. of indep reflcns | 5452 | 4068 |
| no. of obsd reflcns ($I > 2\sigma(I)$) | 3779 | 2489 |
| no. of refined params | 180 | 190 |
| $R$ | 0.056 | 0.062 |
| $R_w$ ($w = 1/\sigma^2(F_o)$) | 0.066 | 0.038 |
| resid electron dens, e Å$^{-3}$ | 0.76 | 0.74 |
| structure solution | heavy-atom method | heavy-atom method |

[a] H atom positions were calculated (except for C(9) where they were omitted) and kept fixed in the final refinement stage, Cp rings 50:50 disordered. [b] H atom positions were calculated (except for C(9) where they were omitted) and kept fixed in the final refinement stage.

**Synthesis of Cp$_2$Zr($\mu$-$\eta^1$:$\eta^2$-C$_6$H$_8$)($\mu$-CH$_3$)GaMe$_2$ (6a).** A solution of trimethylgallium (240 mg, 2.09 mmol) in 3 mL of toluene is added to 200 mg (0.53 mmol) of the (cyclohexyne)(trimethylphosphane)-zirconocene complex **4a** dissolved in 5 mL of toluene. The mixture is stirred for 1 h at room temperature and then all volatiles are removed in vacuo. Residual volatile material is removed by pumping on the residue (10$^{-2}$ mbar) for several hours at 30–35 °C to give 220 mg (98%) of **6a**: mp 138 °C dec; $^1$H NMR (benzene-$d_6$) $\delta$ 5.28 (s, 10 H, Cp), 2.50 (m, 2 H, CH$_2$), 2.39 (m, 2 H, CH$_2$), 1.53 (m, 4 H, 2 CH$_2$), –0.02 (s, 6 H, GaMe$_2$), –0.22 (s, 3 H, $\mu$-CH$_3$); $^{13}$C NMR (benzene-$d_6$) $\delta$ 197.3 (Zr—C=), 109.3 (C$_{planar}$), 108.7 (Cp), 35.0, 29.8 (2 × CH$_2$), 25.2 (2 CH$_2$), –3.1 (GaMe$_2$), –17.2 ($\mu$-CH$_3$); IR (KBr) $\nu$ 3107 cm$^{-1}$, 1444, 1016, 804 (Cp), 1579 (C=C). Anal. Calcd for C$_{19}$H$_{27}$GaZr (416.4): C, 54.81; H, 6.54. Found: C, 53.59; H, 6.64. For details of the X-ray crystal structure determination of **6a** (crystals from pentane) see Table III.

**Synthesis of Cp$_2$Zr($\mu$-$\eta^1$:$\eta^2$-C$_6$H$_4$)($\mu$-CH$_3$)GaMe$_2$ (6b).** Trimethylgallium (480 mg, 4.18 mmol) is dissolved in 5 mL of toluene and added to a solution of 500 mg (1.34 mmol) of the (aryne)(PMe$_3$) metallocene complex **4b** in 10 mL of toluene. The mixture is stirred for 30 min at ambient temperature. The volatile materials are evaporated in vacuo together with the solvent. The remaining oil is freed from any volatiles by pumping on it for several hours at 35 °C to give 540 mg (98%) of **6b**: mp 63 °C (dec., DSC); $^1$H NMR (benzene-$d_6$) $\delta$ 8.01 (m, 1 H, arom CH), 7.54 (m, 1 H, arom CH), 7.24 (m, 2 H, 2 × arom CH), 5.24 (s, 10 H, Cp), 0.11 (s, 6 H, GaMe$_2$), –0.21 (s, 3 H, $\mu$-CH$_3$); $^{13}$C NMR (benzene-$d_6$) $\delta$ 187.3 (Zr—C=), 136.1 ($^1J_{CH}$ = 156 Hz, arom *C*H), 132.2 ($^1J_{CH}$ = 162 Hz, arom *C*H), 128.2 ($^1J_{CH}$ = 157 Hz, 2 × arom *C*H), 117.3 (C$_{planar}$), 109.2 ($^1J_{CH}$ = 174 Hz, Cp), –1.4 ($^1J_{CH}$ = 120 Hz, GaMe$_2$), –14.5 ($^1J_{CH}$ = 121 Hz, $\mu$-CH$_3$); IR (KBr) $\nu$ 3087 cm$^{-1}$, 1440, 1013, 809 (Cp), 1533, 1422, 1407. Anal. Calcd for C$_{19}$H$_{23}$GaZr (412.3): C, 55.35; H, 5.62. Found: C, 53.46; H, 5.41. For details of the X-ray crystal structure determination of complex **6b** (crystals from pentane) see Table III.

**Preparation of Cp$_2$Zr($\mu$-$\eta^1$:$\eta^2$-PhCCH)($\mu$-Cl)GaMe$_2$ (9).** (Phenylethynyl)gallium dimethyl (**7**, 600 mg, 2.99 mmol) is dissolved in 5 mL of toluene and added to a suspension of 750 mg (2.91 mmol) of the

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(20) Erker, G.; Engel; Dorf, U.; Atwood, J. L.; Hunter, W. E. *Angew. Chem.* **1982**, *94*, 915. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 914.

(21) Jeffery, E. A.; Mole, T. *J. Organomet. Chem.* **1968**, *11*, 393.

*J. Am. Chem. Soc.* **1992**, *114*, 8536–8544

oligomeric $[Cp_2Zr(H)Cl]_x$ (**8**) in 10 mL of toluene. The mixture is stirred for 2 h at room temperature. Solvent is then removed from the resulting clear dark-red solution in vacuo. The remaining residue is recrystallized from pentane to give 0.80 g (62%) of **9**: mp 68 °C (dec., DSC); $^1$H NMR (benzene-$d_6$) $\delta$ 7.45 (s, 1 H, =CH), 7.19–7.16, 7.10–7.03 (m, 5 H, Ph), 5.74 (s, 10 H, Cp), 0.20 (s, 6 H, $GaMe_2$); $^{13}$C NMR (benzene-$d_6$) $\delta$ 258.9 (Zr—C=), 146.8 ($^1J_{CH}$ = 154 Hz, = *C*H), 142.8 (ipso-C, phenyl), 129.0, 126.6, 126.3 (*C*H, phenyl), 111.5 ($^1J_{CH}$ = 173 Hz, Cp), −1.3 ($^1J_{CH}$ = 124 Hz, $GaMe_2$); IR (KBr) $\nu$ 1437 cm$^{-1}$, 1013, 801 (Cp), 1589 (C=C).

**Exchange Reactions of Complexes 6a and 6b with Olefins.** (a) Reaction of $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_8)(\mu\text{-}CH_3)GaMe_2$ (**6a**) with norbornene: A sample of **6a** (20 mg, 0.048 mmol) is dissolved in 0.7 mL of benzene-$d_6$. Norbornene (5 mg, 0.053 mmol) is added, and the progress of the reaction monitored by $^1$H NMR spectroscopy. Trimethylgallium ($^1$H NMR $\delta$ −0.15, s) and the product **13** are formed. After 1 h at ambient temperature the reaction has almost gone to completion. The sealed NMR tube is opened. The volatile materials are removed from the orange-colored solution in vacuo, and the residue is washed with a small volume of cold pentane. A yellow solid of **13** is obtained (10 mg, 50% yield): mp 173 °C (dec., DSC). The identification as **13** was carried out spectroscopically: $^1$H NMR (benzene-$d_6$) $\delta$ 5.89, 5.85 (each s, 5 H, Cp), 2.40 (m, 1 H), 2.33 (m, 1 H), 2.11 (m, 2 H), 1.67 (m, 4 H), 1.57 (m, 2 H), 1.46 (m, 4 H), 1.25 (m, 4 H); $^{13}$C NMR (benzene-$d_6$) $\delta$ 181.0, 137.6 (olefinic C), 111.5 (Cp), 67.9, 51.9, 45.5, 40.1 (each *C*H), 36.6, 35.7, 34.5, 31.1, 29.9, 24.8, 24.5 (each *C*$H_2$).

(b) Reaction of $Cp_2Zr(\mu\text{-}\eta^1{:}\eta^2\text{-}C_6H_4)(\mu\text{-}CH_3)GaMe_2$ (**6b**) with ethylene: The complex **6a** (20 mg, 0.049 mmol) is dissolved in 0.6 mL of benzene-$d_6$. Ethylene is bubbled through the solution in a 5-mm NMR tube for 10 min. The NMR tube is then sealed, and the reaction is allowed to proceed for 1 h. An $^1$H NMR spectrum revealed the presence of excess ethylene (s at $\delta$ 5.24) and the formation of the zirconaindane **14**: $^1$H NMR (benzene-$d_6$) $\delta$ 7.05 (m, 4 H, $C_6H_4$), 5.86 (s, 10 H, Cp), 3.32 (pseudo-t, 2 H, $CH_2$), 1.29 (pseudo-t, 2 H, $CH_2$). After 36 h the formation of **15** as an additional reaction product was revealed by its $^1$H NMR signals.

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**Supplementary Material Available:** Details of the X-ray crystal structure analysis of **6a** and **6b** including atomic coordinates and complete listings of bond lengths and angles (17 pages); listings of observed and calculated structure factors (30 pages). Ordering information is given on any current masthead page.

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# MM3 Molecular Mechanics Study of Alkylphosphines

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**Abstract:** The MM3 force field has been extended to cover alkylphosphines. The structures of eight alkylphosphines have been reproduced, as well as the known conformational equilibria, barriers to rotation, moments of inertia, and dipole moments. The vibrational spectra for these eight compounds have been studied and fit with a root mean square error of 34 cm$^{-1}$.

## Introduction

The recently reported MM3 force field can accurately handle a wide range of organic functional groups, including saturated hydrocarbons,[1] alkenes,[2] aromatic hydrocarbons,[3] aliphatic amines,[4] amides and polypeptides,[5] alcohols and ethers,[6] aldehydes and ketones,[7] nitro compounds,[8] sulfides,[9] and disulfides.[10] The present work has centered on developing MM3 force field parameters to properly model alkylphosphines.

The extension of the earlier MM2 force field to treat most functional groups has been progressing since its introduction almost 15 years ago. Because of this effort the MM2 force field has been widely used. In time the MM3 force field will be able to treat as many classes of compounds as its predecessor. Due to the use of more complex potential functions and the addition of torsion–stretch and generic bend–bend interaction parameters, MM3 has the ability to reproduce vibrational spectra. This is one of the major innovations of MM3 over MM2. Reproducing the spectral data, as well as the inclusion of these additional terms, makes parameterization of the MM3 force field somewhat more complex than it was for MM2, but the additional parameters have been shown to be necessary in order to accurately reproduce the experimental vibrational data.[1]

As an initial step to the parameterization of biologically important phosphorus compounds, such as phosphates and nucleotides, we have studied alkylphosphines in order to develop a force field capable of calculating the structures, relative energies, and vibrational spectra of this class of compounds. The phosphine parameter set developed in this work, presented as Table I, has been optimized to reproduce structure, vibrational spectra, rotational barriers, moments of inertia, and dipole moments.[11] These parameters have been incorporated into the MM3(92) program.[12]

## Methods

Experimental structural data were found in the literature for phosphine,[13] methylphosphine,[14,15] dimethylphosphine,[15] trimethylphosphine,[16]

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[1] Allinger, N. L.; Yuh, Y. H.; Lii, J.-H. *J. Am. Chem. Soc.* **1989**, *111*, 8551.

[2] Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8566.

[3] Lii, J.-H.; Allinger, N. L. *J. Am. Chem. Soc.* **1989**, *111*, 8576.

[4] Schmitz, L. R.; Allinger, N. L. *J. Am. Chem. Soc.* **1990**, *112*, 8307.

[5] Lii, J.-.H.; Allinger, N. L. *J. Comput. Chem.* **1991**, *12*, 186.

[6] Allinger, N. L.; Rahman, M.; Lii, J.-H. *J. Am. Chem. Soc.* **1990**, *112*, 8293.

[7] Allinger, N. L.; Chen, K.; Rahman, M.; Pathiaseril, A. *J. Am. Chem. Soc.* **1991**, *113*, 4505.

[8] Allinger, N. L.; Kuang, J.; Thomas, H. D. *J. Mol. Struct.* **1990**, *209*, 125.

[9] Allinger, N. L.; Quinn, M.; Rahman, M.; Chen, K. *J. Phys. Org. Chem.*, in press.

[10] Chen, K.; Allinger, N. L. *J. Phys. Org. Chem.*, in press.

[11] All of the phosphine parameters that are included in the original MM3 program (MM3(91)) and indicated by a ** are carried over from preliminary work and are superseded by the parameters herein.

[12] A parameter set for use with MM3(91) is also available upon request from the authors.

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