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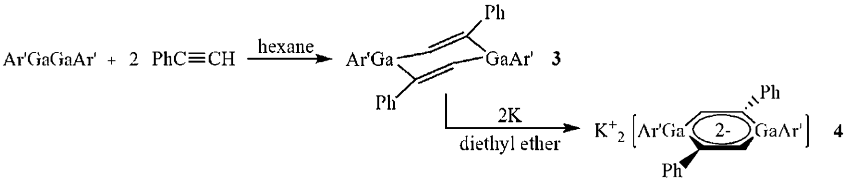
Gallium Chemistry (1)

Synthesis and Characterization of $[Ar'GaC(Ph)CH]_2$ and $K_2[Ar'GaC(Ph)CH]_2{\cdot}OEt_2$: From Digallene to Digallacyclohexadiene to Digallatabenzene[**]

*Zhongliang Zhu, Xinping Wang, Marilyn M. Olmstead, and Philip P. Power**

Metallabenzenes are compounds in which one or more of the benzene carbons are replaced by a metal or metal-centered group. They are of interest because of the effects of the metal on delocalization and reactivity.[1] Beginning with an osmabenzene in 1982,[2] numerous transition-element metallabenzenes have been characterized.[1a,b] There is also a growing interest in their main-group metal counterparts.[1c–e] The latter area originated in the inclusion of phosphorus,[3] antimony,[3,4] bismuth[4] or boron[5] in benzene rings in the 1960s and 1970s. More recently, several compounds in which one or more of the heavier Group 14 elements silicon, germanium, or tin form part of a benzene or naphthalene ring have been reported.[6] Although some Group 13 metal clusters that incorporate three- or four-membered all-metal dianionic aromatic rings as in $M_2'(MAr^{\#})_3$ ($M'/M = Na/Al$,[7a] Na/Ga,[7b] or K/Ga;[7c] $Ar^{\#} =$ 2,6-$Mes_2C_6H_3$) or $K_2Ga_4Ar^{*}_2$[7d] ($Ar^{*} = 2,6\text{-}(2,4,6\text{-}iPr_3C_6H_2)_2C_6H_3$) are known, a well-characterized metallabenzene incorporating a Group 13 metal has been isolated only as the transition-metal-complexed species $[Mn(CO)_3(\eta^5\text{-}C_5H_5GaMes^{*})]$ (**1**; $Mes^{*} = 2,4,6\text{-}tBu_3C_6H_2$).[8] The related gallacyclopentadienyl transition-metal complex $[Co(\eta^5\text{-}C_5H_5)(\eta^5\text{-}C_4H_4GaMes^{*})]$[9] and a base-stabilized dibenzogallepin[10] have also been reported. In **1**, the gallatabenzene anion $[C_6H_5GaMes^{*}]^-$, which was characterized in solution, is effectively η^5-bound by the five ring-carbon atoms to the manganese such that the GaC_5 ring is nonplanar, with a fold angle of 34.5° between the C_5 and C_2Ga planes indicating disruption of delocalization. Herein, we describe a new route to an essentially planar delocalized metallabenzene incorporating two Group 13 metals by treatment of a "digallene" Ar′GaGaAr′ (**2**)[11] with an alkyne to give the 1,4-digallacyclohexadiene $[Ar'GaC(Ph)CH]_2$ (**3**, Scheme 1), which, upon reduction with potassium, affords the 1,4-digallatabenzene salt $K_2[Ar'GaC(Ph)CH]_2{\cdot}OEt_2$ (**4**).



Scheme 1. Synthetic route to $[Ar'GaC(Ph)CH]_2$ (**3**) and $K_2[Ar'GaC(Ph)CH]_2{\cdot}OEt_2$ (**4**). $Ar' = 2,6\text{-}(2,6\text{-}iPr_2C_6H_3)_2C_6H_3$.

Treatment of a hexane solution of the "digallene" Ar′GaGaAr′ with two equivalents of phenylacetylene rapidly discharged the green color within 30 min. Concentration and cooling afforded colorless crystals of **3** in good yield. A diethyl ether solution of **3** was reduced with potassium to afford a deep blue solution, which upon cooling gave **4** as black needles in moderate yield. Compound **3** and **4** were characterized spectroscopically and by X-ray crystallography.[12]

The reaction of Ar′GaGaAr′ with HC≡CPh occurs readily to give the new six-membered-ring product **3**. The structure of **3** (Figure 1) shows that the $\{C_4Ga_2\}$ ring has a distorted, flattened-chair conformation. The fold angle between the C31-C32-C31A-C32A and C31A-Ga1-C32 planes is 14.8°, and the core Ga–C distances are 1.959(2) and 1.967(2) Å, with a C-Ga-C internal ring angle of 115.26(7)°. The Ga–C1 distance to the Ar′ group is slightly longer than the Ga–C ring distances, suggesting some π conjugation between gallium

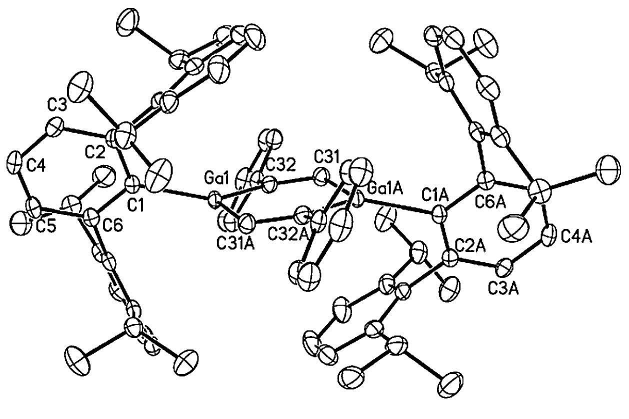


Figure 1. Plot of **3** with thermal ellipsoids set at 50% probability and hydrogen atoms removed for clarity. Selected bond lengths [Å] and angles [°]: Ga1–C1 1.991(2), Ga1–C32 1.967(2), Ga1A–C31 1.959(2), C32–C31 1.353(2), C32–C33 1.490(2), C1–C2 1.407(2); C32-Ga1-C31A 115.26(7), C31-C32-Ga1 114.9(1), C32-C31-Ga1A 127.44(13), C31-C32-C33 119.3(2), Ga1-C32-C33 125.8(1), C32-Ga1-C1 132.40(7), C31A-Ga1-C1 111.27(7), Ga1-C1-C2 115.93(11).

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[*] Z. Zhu, Dr. X. Wang, Prof. M. M. Olmstead, Prof. P. P. Power
Department of Chemistry, University of California
One Shields Avenue, Davis, CA 95616 (USA)
Fax: (+1) 530-752-8995
E-mail: pppower@ucdavis.edu

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and the core carbon atoms. The C31−C32 bond length is 1.353(2) Å, which is typical for a C=C double bond. The Ga1-C32-C31 and Ga1A-C31-C32 angles are 114.9(1) and 127.4(1)°, which is probably due to the different carbon substituents. The transannular Ga···Ga separation is 3.422 Å, which indicates that there is no interaction between the metal centers.

The addition of unsaturated molecules, such as an alkene or alkyne, to low-valent Group 13 metal species is rare.[11,13] With acetylene, the Al^I species :AlL (L = $[(2,6\text{-}i\mathrm{Pr}_2\mathrm{C}_6\mathrm{H}_3)\mathrm{N}{=}\mathrm{CMe}]_2\mathrm{CH}$) forms $\mathrm{LAl}(\eta^2\text{-}\mathrm{C}_2\mathrm{H}_2)$ at low temperature.[13a] However, the reaction of :AlL with a bulkier alkyne did not occur, and reactions involving Group 13 metals and substituted alkynes have been observed using only M^{III} starting materials under reducing conditions. For instance, the reduction of $\mathrm{LAlI_2}$ with potassium in the presence of an alkyne such as $\mathrm{Me_3SiC{\equiv}CSiMe_3}$ afforded the cyclopropene $[\mathrm{LAl}(\eta^2\text{-}\mathrm{Me_3SiCCSiMe_3})]$,[13b] and reductions using $\mathrm{Ar'AlI_2}$ afforded the dimetallacyclobutene $\mathrm{Ar'A\overline{lC(SiMe_3)C(SiMe_3)Al}Ar'}$.[13c]

The double reduction of **3** with potassium gave **4**, and the structure was determined by X-ray crystallography (Figure 2). It features a planar $\{\mathrm{GaC(Ph)CH}\}_2^{2-}$ six-π-electron ring with two potassium ions located above and below the centroid (K1−centroid = 2.738(9) Å and K2−centroid = 2.745(9) Å). Within the core, the Ga1−C61, Ga1−C64, Ga2−C62, and Ga2−C63 distances are 1.899(2), 1.934(2), 1.941(2), and 1.910(2) Å, respectively, which are all shorter than the average Ga−C distance of 1.963(4) Å in **3**, suggesting some multiple-bond character. In contrast, the Ga1−C1 and Ga2−C31 distances to the Ar′ substituents (1.982(2) and 1.997(2) Å) are essentially unchanged from the 1.991(2) Å in **3**. The C−C bonds within the core are 1.418(3) and 1.408(3) Å, and are thus lengthened by ca. 0.06 Å in comparison to **3** (1.353(2) Å). These distances are similar to the C−C bond lengths in aromatic rings,[1,14] and are consistent with the delocalization of π electrons within the $\{\mathrm{C_4Ga_2}\}$ core in **4**. Narrower C-Ga-C internal ring angles of 112.98(9) and 112.27(9)° were observed, and the Ga1-C61-C62, Ga1-C64-C63, Ga2-C63-C64, and Ga2-C62-C61 angles are 129.9(2), 117.0(2), 130.4(2), and 117.2(2)°, which is consistent with the different substitution at each pair of carbon atoms. The planes of the central rings of the Ar′ ligands are orientated almost perpendicularly to the $\{\mathrm{GaC(Ph)CH}\}_2^{2-}$ unit. The potassium ion K1 is also complexed by two flanking aryl rings, one from each of the terphenyl ligands, which produces a slight tilting of the Ar′ substituents toward each other, and K2 is coordinated by a diethyl ether oxygen. The planar geometry of the core in **4** may be contrasted with several transition-element dimetallabenzenes,[15] for example, 1,3-diniobiabenzenes and 1,3-ditantalabenzenes, which are nonplanar, indicating a weakened π-orbital overlap.

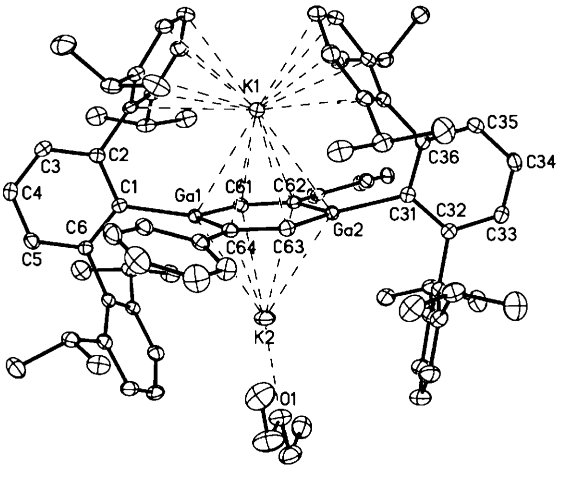
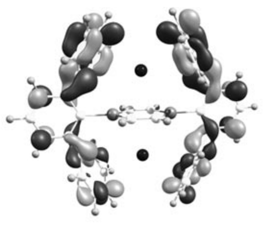
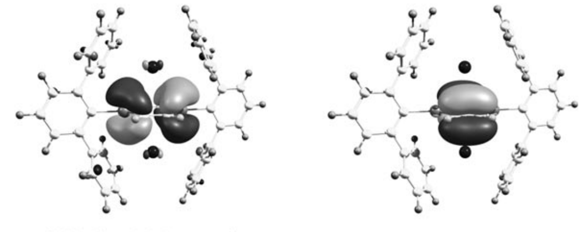


Figure 2. Plot of **4** with thermal ellipsoids set at 50% probability and hydrogen atoms omitted for clarity. Selected bond lengths [Å] and angles [°]: Ga1–C1 1.982(2), Ga1–C61 1.899(2), Ga1–C64 1.934(2), C61–C62 1.418(3), C63–C64 1.408(3), K1–centroid(1,4-digallabenzene) 2.738(9), K2–centroid(1,4-digallabenzene) 2.745(9), K1–centroid(C7–C12) 2.99(1), K1–centroid(C43–C48) 2.92(1), K2–O1 2.638(2); C61-Ga1-C64 112.98(9), C62-C61-Ga1 129.9(2), C63-C64-Ga1 117.02(15), C61-Ga1-C1 121.59(9), C64-Ga1-C1 124.94(8), Ga1-C1-C2 121.1(2). Mean deviation in 1,4-digallabenzene ring: 0.0168 Å. Dihedral angles [°] between planes: C1–C6 and C31–C36, 4.5; 1,4-digallabenzene ring and C1–C6/C31–C36 plane: 97.3/93.5; 1,4-digallabenzene ring and phenyl rings at C62/C64: 21.3/17.9

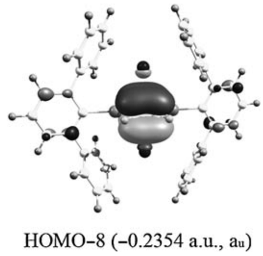
DFT calculations on a simple model, $\mathrm{K_2[ArGaCHCH]_2}$ (Ar = 2,6-$\mathrm{Ph_2C_6H_3}$; Figure 3), performed at B3LYP/6-31G* level gave structural parameters that are in good agreement with experimental values and further supported the aromatic character of **4**.[16] There are three occupied MOs of π symmetry at the $\{\mathrm{GaCHCH}\}_2^{2-}$ ring. The HOMO–8 has a_u symmetry, and the HOMO–2 and HOMO are of b_g symmetry



LUMO (−0.0231 a.u., a_u)



HOMO (−0.0857 a.u., b_g) HOMO–2 (−0.2073 a.u., b_g)



HOMO–8 (−0.2354 a.u., a_u)

Figure 3. Key frontier molecular orbitals of the model species for **4**, $\mathrm{K_2[(2,6\text{-}Ph_2C_6H_3)GaCHCH]_2}$, calculated by DFT.

with one phase change. There is a relatively large energy difference (ca. 0.12 a.u.) between the HOMO and HOMO–2 owing to their location on different groups of ring atoms. The LUMO is mainly a ligand-based MO with a_u symmetry, and the energy separation of ca. 0.063 a.u. between HOMO and LUMO is consistent with the strong absorption in the UV/Vis spectrum of **4** at 782 nm (0.058 a.u.). The ^{1}H NMR spectra for **3** and **4** both revealed a downfield shift of the ring proton at $\delta = 7.32$ ppm and 8.48 ppm, respectively. The downfield shift of the former signal may be due primarily to the metal-based anisotropic effect; however, the latter signal, which is even further downfield, is consistent with the presence of an aromatic ring current within the digallatabenzene ring in **4**.

In conclusion, the digallatabenzene **4** has been synthesized from the corresponding digallacyclohexadiene **3** by a two-electron-reduction with potassium metal. A planar six-membered $\{Ga_2C_4\}$ ring together with shortened Ga–C and lengthened C–C distances support the view that **4** is a Group 13 benzene analogue with 6π delocalized electrons. DFT calculations and ^{1}H NMR spectroscopy also support the aromatic character in **4**. The above reactions underline the utility of Ar′GaGaAr′ as a starting material,[11] which can also react directly with H_2 or NH_3 under mild conditions to give hydride or amide products.[17]

Experimental Section

All manipulations were carried out under anaerobic and anhydrous conditions. ^{1}H and ^{13}C NMR spectra were recorded on a Varian 600 spectrometer and referenced to known standards.

[Ar′GaC(Ph)CH]$_2$ (**3**): PhC≡CH (0.37 mL, 3.21 mmol) was added dropwise to Ar′GaGaAr′ (1.50 g, 1.60 mmol) in hexane (80 mL) with rapid stirring to afford a white precipitate of crude **3** within 30 min. Yield: 1.30 g, 76 %; m.p. 297–298 °C. X-ray quality crystals of **3** were grown from *n*-hexane. ^{1}H NMR (600 MHz, C_6D_6, 25 °C): $\delta = 1.07$ (d, 48 H, *o*-CH(C*H*$_3$)$_2$, $^{3}J_{HH} = 6.6$ Hz), 3.12 (sept, 8 H, C*H*(CH$_3$)$_2$, $^{3}J_{HH} = 6.6$ Hz), 6.96–6.99 (m, 2 H, *p*-Ph-C=CH), 7.04–7.01 (m, 4 H, *m*-Ph-C=CH), 7.02 (d, 4 H, *m*-C_6H_3, $^{3}J_{HH} = 6.0$ Hz), 7.09 (d, 8 H, *m*-Dipp, $^{3}J_{HH} = 7.8$ Hz), 7.21 (t, 4 H, *p*-Dipp, $^{3}J_{HH} = 7.8$ Hz), 7.26–7.29 (m, 2 H, *p*-C_6H_3) 7.32 (s, 2 H, C*H*=CPh), 7.32 ppm (dd, 4 H, *o*-Ph-C=CH, $^{3}J_{HH} = 7.2$ Hz, $^{4}J_{HH} = 1.2$ Hz). ^{13}C {^{1}H} NMR (C_6D_6, 150.9 MHz, 25 °C): $\delta =$ 22.7 (*o*-CH(*C*H$_3$)$_2$), 26.7 (*o*-CH(*C*H$_3$)$_2$), 30.7 (*o*-*C*H(CH$_3$)$_2$), 123.6, 127.0, 128.0, 128.1, 128.4, 128.8, 129.0, 141.1, 145.8, 146.4, 147.3, 161.2 ppm (*PhC*=*C*H and Ar*C*).

K$_2$[Ar′GaC(Ph)CH]$_2$·OEt$_2$ (**4**): A solution of **3** (0.6 g, 0.56 mmol) in diethyl ether (70 mL) was added to finely cut potassium (0.044 g, 0.56 mmol) at ca. 25 °C. Stirring overnight gave a deep blue solution, which was then concentrated to ca. 30 mL. Cooling to ca. –18 °C gave crystals of **4** as black needles. Yield: 0.39 g, 56.9 %; m.p. > 300 °C. ^{1}H NMR (600 MHz, C_6D_6, 25 °C): $\delta = 0.74$ (d, 6 H, *o*-CH(C*H*$_3$)$_2$, $^{3}J_{HH} = 6.6$ Hz), 1.01 (d, 6 H, *o*-CH(C*H*$_3$)$_2$, $^{3}J_{HH} = 6.6$ Hz), 1.11 (t, 6 H, (C*H*$_3$CH$_2$)$_2$O, $^{3}J_{HH} = 7.2$ Hz), 1.23 (d, 6 H, *o*-CH(C*H*$_3$)$_2$, $^{3}J_{HH} = 7.2$ Hz), 1.47 (d, 6 H, *o*-CH(C*H*$_3$)$_2$, $^{3}J_{HH} = 7.2$ Hz), 2.25 (q, 4 H, (CH$_3$C*H*$_2$)$_2$O, $^{3}J_{HH} = 7.2$ Hz), 3.41 (sept, 2 H, C*H*(CH$_3$)$_2$, $^{3}J_{HH} = 6.6$ Hz), 3.51 (sept, 2 H, C*H*(CH$_3$)$_2$, $^{3}J_{HH} = 6.6$ Hz), 6.67 (t, 4 H, *m*-Ph-C=CH, $^{3}J_{HH} = 7.8$ Hz), 6.78 (dd, 4 H, *m*-Dipp, $^{3}J_{HH} = 7.8$ Hz, $^{4}J_{HH} = 1.2$ Hz), 6.84 (dd, 4 H, *m*-Dipp, $^{3}J_{HH} = 7.8$ Hz, $^{4}J_{HH} = 0.6$ Hz), 6.87 (t, 2 H, *p*-C_6H_3, $^{3}J_{HH} = 6.6$ Hz), 7.15 (t, 4 H, *p*-Dipp, $^{3}J_{HH} = 7.5$ Hz), 7.22–7.25 (m, 6 H, *o*-Ph-C=CH and *p*-Ph-C=CH), 7.73 (d, 4 H, *m*-C_6H_3, $^{3}J_{HH} = 7.8$ Hz), 8.48 ppm (s, 2 H, C*H*=CPh); ^{13}C {^{1}H} NMR (C_6D_6, 100.6 MHz, 25 °C): $\delta = 15.6$ ((*C*H$_3$CH$_2$)$_2$O), 23.0 (CH(*C*H$_3$)$_2$), 23.7 (CH(*C*H$_3$)$_2$), 25.4 (CH(*C*H$_3$)$_2$), 26.5 (CH(*C*H$_3$)$_2$), 30.9 (*C*H(CH$_3$)$_2$), 31.2 (*C*H(CH$_3$)$_2$), 65.9 ((CH$_3$*C*H$_2$)$_2$O), 121.6, 121.8, 122.7, 125.2, 126.0, 127.9, 128.2, 128.8, 143.2, 147.0, 147.1, 148.8, 149.7, 151.1, 160.1, 164.7 ppm (*PhC*=*C*H and Ar*C*). UV/Vis (*n*-hexane) λ_{max} (ε): 782 nm (9100 mol L^{-1} cm^{-1}).

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[1] a) J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205; b) C. W. Landorf, M. M. Haley, *Angew. Chem.* **2006**, *118*, 4018; *Angew. Chem. Int. Ed.* **2006**, *45*, 3914; c) Y. Z. Wang, G. H. Robinson, *Organometallics* **2007**, *26*, 2; d) N. Tokitoh, *Acc. Chem. Res.* **2004**, *37*, 86; e) V. Y. Lee, A. Sekiguchi, *Angew. Chem.* **2007**, *119*, 6716; *Angew. Chem. Int. Ed.* **2007**, *46*, 6596.

[2] a) G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811; b) G. P. Elliott, N. M. McAuley, W. R. Roper, *Inorg. Synth.* **1989**, *26*, 184.

[3] G. Märkl, *Angew. Chem.* **1966**, *78*, 907; *Angew. Chem. Int. Ed. Engl.* **1966**, *5*, 846.

[4] A. J. Ashe III, *Acc. Chem. Res.* **1978**, *11*, 153.

[5] A. J. Ashe III, P. Shu, *J. Am. Chem. Soc.* **1971**, *93*, 1804.

[6] See references in reviews [1d] and [1e], and in: R. Kinjo, M. Ichinohe, A. Sekiguchi, N. Takagi, M. Sumimoto, S. Nagase, *J. Am. Chem. Soc.* **2007**, *129*, 7766.

[7] a) R. J. Wright, M. Brynda, P. P. Power, *Angew. Chem.* **2006**, *118*, 6099; *Angew. Chem. Int. Ed.* **2006**, *45*, 5953; b) X.-W. Li, W. T. Pennington, G. H. Robinson, *J. Am. Chem. Soc.* **1995**, *117*, 7578; c) X.-W. Li, Y. Xie, P. R. Schreiner, K. D. Gripper, R. C. Crittendon, C. F. Campana, H. F. Schaefer, G. H. Robinson, *Organometallics* **1996**, *15*, 3798; d) B. Twamley, P. P. Power, *Angew. Chem.* **2000**, *112*, 3643; *Angew. Chem. Int. Ed.* **2000**, *39*, 3500.

[8] A. J. Ashe III, S. Al-Ahmad, J. W. Kampf, *Angew. Chem.* **1995**, *107*, 1479–1481; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1357.

[9] A. H. Cowley, F. P. Gabbaï, A. Decken, *Angew. Chem.* **1995**, *107*, 1429; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1370.

[10] B. Quillian, Y.-Z. Wang, P.-R. Wei, C. S. Wannere, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2007**, *129*, 13380.

[11] N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667.

[12] Crystallographic data recorded at 90 K with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). **3**: $a = 11.3057(9)$, $b = 11.6393(9)$, $c = 23.807(2)$ Å, $\beta = 95.950(2)°$, monoclinic, space group $P2_1/n$, $Z = 2$, $R1 = 0.0310$ for 5955 ($I > 2\sigma(I)$) data, w$R2$ (all data) = 0.0825; **4**: $a = 13.933(3)$, $b = 14.800(3)$, $c = 21.634(4)$ Å, $\alpha = 97.140(14)$, $\beta = 109.722(19)$, $\gamma = 110.349(13)°$, triclinic, space group $P\bar{1}$, $Z = 2$, $R1 = 0.0441$ for 31 305 ($I > 2\sigma(I)$) data, w$R2$ (all data) = 0.1114. CCDC-710216 (**3**) and CCDC-710217 (**4**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[13] a) C. Cui, S. Köpke, R. Herbst-Irmer, H. W. Roesky, M. Noltemeyer, H.-G. Schmidt, B. Wrackmeyer, *J. Am. Chem. Soc.* **2001**, *123*, 9091; b) H. Zhu, J. Chai, H. Fan, H. W. Roesky, C. He, V. Jancik, H.-G. Schmidt, M. Noltemeyer, W. A. Merrill, P. P. Power, *Angew. Chem.* **2005**, *117*, 5220; *Angew. Chem. Int. Ed.* **2005**, *44*, 5090; c) C. Cui, X. Li, C. Wang, J. Zhang, J. Cheng, X. Zhu, *Angew. Chem.* **2006**, *118*, 2303; *Angew. Chem. Int. Ed.* **2006**, *45*, 2245.

[14] a) V. I. Minkin, M. N. Glukhovtsev, B. Y. Simkin, F. Weinhold, C. R. Landis, *Aromaticity and Antiaromaticity. Electronic and Structural Aspects*, Wiley, New York, **1994**, p. 38; b) T. M. Krygowski, M. K. Cyrański, *Chem. Rev.* **2001**, *101*, 1385, and the references therein.

[15] a) R. D. Profilet, P. E. Fanwick, I. P. Rothwell, *Angew. Chem.* **1992**, *104*, 1277; *Angew. Chem. Int. Ed. Engl.* **1992**, *31*, 1261; b) P. N. Riley, R. D. Profilet, M. M. Salberg, P. E. Fanwick, I. P. Rothwell, *Polyhedron* **1998**, *17*, 773.

[16] DFT calculations were performed at the B3LYP/6-31G* level using simplified models based on the X-ray diffraction structure of **3**, in which isopropyl groups of the flanking aryls were replaced with H and Et_2O was omitted. Calculations were performed with the Gaussian 03 package (M. J. Frisch et al., Gaussian 03, Revision B.03; Gaussian, Inc.: Pittsburgh, PA, **2003**; see Supporting Information for full reference and detailed calculation method), and the representations of the molecular orbitals were generated with the Chemcraft program (Grigoriy A. Zhurko., http://www.chemcraftprog.com/index.html).

[17] Z. L. Zhu, X. Wang, Y. Peng, H. Lei, J. C. Fettinger, E. Rivard, P. P. Power, *Angew. Chem.* **2009**, *48*, 2065; *Angew. Chem. Int. Ed.* **2009**, *48*, 2031.