Gallium Ligands

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Methylgallium as a Terminal Ligand in $[(Cp^*Ga)_4Rh(GaCH_3)]^{+}$**

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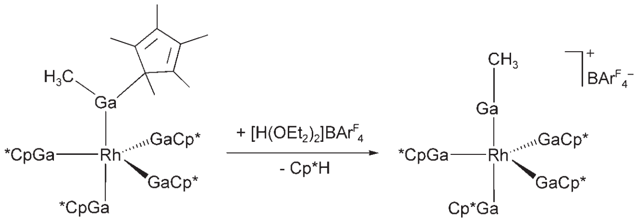
Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 60th birthday

As “exotic” ligands at transition-metal centers M, carbenoid Group 13 metal compounds ER (E = Al, Ga, In; R = bulky substituent: e.g. alkyl, aryl, C_5Me_5 (Cp*), bisketoiminates, amidinates, guanidinates) are attracting a great deal of attention because their properties can be compared with those of the related borylenes[1a,b] and N-heterocyclic carbenes (NHCs).[1c–f] In particular, complexes with ECp* ligands show interesting reactivity that is related to the soft binding properties and facile haptotropic shifts of the Cp* ring, which allows a modulation of the electrophilicity at the Group 13 center E.[2] Accordingly, even selective protolysis of coordinated GaCp* is possible: the treatment of the complex $[Pt(GaCp^*)_4]$ with $[H(OEt_2)_2]BAr^F_4$ ($Ar^F = 3,5\text{-}(CF_3)_2C_6H_3$) yields the dimer $[Pt_2H(Ga)(GaCp^*)_7]^{2+}$ by elimination of Cp*H via the intermediate $[GaCp^*)_4PtH]^+$. By using the Ga^+ transfer reagent $[Ga_2Cp^*]^+$, the $[(GaCp^*)_4PtGa]^+$ complex has been generated in which the bonding of naked Ga^+ as a strong σ/π-acceptor ligand without σ-donor properties has been demonstrated.[3] As part of our continuing work in this area, we set out to generate otherwise elusive GaR moieties by protolytic cleavage of Cp*H from coordinated Ga(R)Cp* groups. The choice of the R substituent for isolable and thus synthetically useful monovalent ER compounds is limited because of the inherent instability of E^I and its disproportionation into E^0 and E^{III}.[4] Methylgallium, for example, has to date only been studied by matrix studies at low temperatures.[5] Very few complexes bearing ER ligands with sterically nondemanding groups R without π-donor/acceptor properties, such as the anion $[\{Fe(CO)_4\}_2GaCH_3]^-$ and the dimer $[\{Cp^*IrAlEt\}_2]$, are known.[6,7] However, all these complexes feature the ER ligand in a bridging (tricoordinate) binding mode, which rules out direct comparisons with other dicoordinate (terminal) ER ligands. Analogously, the first terminal alkyl borylene complex, [Cp(CO$_2$)MnB*t*Bu], has been reported recently. The Mn–BR (R = *t*Bu) bond was described as weakly polar but with significant π-backbonding.[1b]

The reaction of $[Rh(CH_3)(cod)(py)]$ with excess of GaCp* in hexane at room temperature leads to the substitution of the labile ligands pyridine (py) and 1,5-cyclooctadiene (cod), as well as to the insertion of the carbenoid GaCp* into the Rh–CH_3 σ bond to give the all-Ga-coordinated neutral complex $[(Cp^*Ga)_4Rh(\eta^1\text{-}Cp^*GaCH_3)]$ (**1**) in 89 % yield (Scheme 1).



1 **2**

Scheme 1. Protolysis of **1** in fluorobenzene.

We have reported and discussed related insertion reactions of ER ligands into Rh–X bonds previously (X = Cl, CH_3).[2a,8] Compound **1** is quite stable at room temperature when stored under inert gas atmosphere (Ar) and dissolves well in all noncoordinating, nonpolar organic solvents such as hexane, benzene, or toluene. The ^1H NMR spectrum at room temperature in C_6D_6 displays two sharp singlets with an integral ratio of approximately 75:3, which split into three signals with an integral ratio close to 15:60:3 in [D$_8$]toluene at −100 °C. This observation is assigned to a fluxional process at room temperature, which leads to the exchange of the CH_3 and/or Cp* groups between all the gallium centers.

Single crystals of **1**, suitable for X-ray diffraction studies, were obtained by slowly cooling a saturated *n*-hexane solution of **1** to −30 °C for 12 h. Compound **1** crystallizes in the tetragonal space group *P*4(2)/*m*. The complex adopts a distorted trigonal-bipyramidal structure in the solid state, which is consistent with the results from low-temperature NMR studies (see the Supporting Information). One GaCp* ligand and the η^1-Cp*GaMe ligand, resulting from the insertion reaction, occupy the axial positions. Surprisingly, the axial Rh–Ga bond lengths are quite similar for η^1-Cp*GaMe (242.98(13) pm) and GaCp* (239.41(13) pm) despite the different coordination. The protolysis of **1** with a stoichiometric amount of pure crystalline $[H(OEt_2)_2]BAr^F_4$ at −30 °C in fluorobenzene solution leads to an immediate color change of the initial red reaction mixture to pale yellow (Scheme 1).

Upon slow diffusion of *n*-hexane into this solution at 25 °C, pale yellow single crystals of the salt $[(Cp^*Ga)_4Rh(GaCH_3)]BAr^F_4$ (**2**) could be isolated in 78 % yield. The

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

^1H NMR spectrum of isolated **2** in a fluorobenzene/C_6D_6 (10:1) mixture at room temperature shows signals for the $BAr^F{}_4{}^-$ ion at $\delta = 8.27$ (ca. 8H) and at 7.56 ppm (ca. 4H), as well as two sharp singlets at $\delta = 1.64$ and 0.54 ppm with an integral ratio of close to 60:3, which suggests a fluxional structure in solution. A single-crystal X-ray diffraction study[9] reveals a distorted trigonal-bipyramidal structure for the cation $[(GaCp^*)_4Rh(GaCH_3)]^+$, in which the desired $GaCH_3$ group occupies an axial position (Figure 1). $GaCH_3$ is the smallest possible GaR ligand (except R = H) and neither steric repulsions nor electronic π effects of the substituent R should effect the M–Ga bond much. Both, the known $[(Cp^*Ga)_4PtGa]^{+}$[3] and the new $[(Cp^*Ga)_4Rh(GaCH_3)]^+$ serve as isoelectronic (18 valence electrons) and basically isostructural models to compare the M–GaR bonding parameters. The striking feature of the structure of $[(Cp^*Ga)_4Rh(GaCH_3)]^+$ is the counterintuitive fact that the Rh–$GaCH_3$ bond (247.11(10) pm) is by far the *longest* Rh–Ga bond in this complex. This Rh–Ga1 bond is about 8% longer than the axial Rh–Ga3 and the equatorial Rh–Ga(2,4,5) bonds, which differ from each other by only 1% (228.15(6)–230.99(7) pm). These Rh–GaCp* bonds in the cation **2** are shorter than those in the neutral compound **1** (239.41(13)–234.76(8) pm).

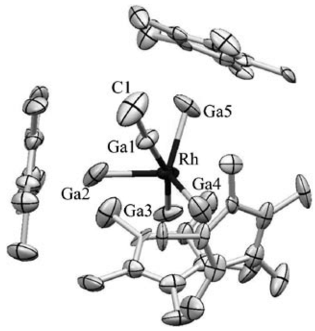

Figure 1. Structure of the cation in **2** (thermal ellipsoids are shown with 50% probability, hydrogen atoms have been omitted for clarity). Selected bond lengths [pm] and angles [°]: Rh-Ga1 247.11(10), Rh-Ga2 230.99(7), Rh-Ga4 228.15(6), Rh-Ga5 228.15(6), Rh-Ga3 230.99(7), Ga1-C1 195.8(11), Ga1-Ga2 276.61(13), Ga1-Ga5 286.83(13); C1-Ga1-Rh 176.1(5), Ga1-Rh-Ga3 163.58(4), Ga2-Rh-Ga4 107.91(2), Ga4-Rh-Ga5 119.59(4).

The isolobal relationship between the fragments L_4Rh and CH_3 suggests that the cation $[(GaCp^*)_4Rh(GaCH_3)]^+$ can be viewed as being composed of a nucleophilic 18-electron fragment $[(GaCp^*)_4Rh]^-$ and an electrophilic $[GaCH_3]^{2+}$ ion, which is similar to the description of $[Ga(CH_3)_2]^+$ as a Ga^{3+} ion and two anionic methyl groups. It should be noted that $[(Cp^*Ga)_4Rh(\eta^1\text{-}Cp^*GaCH_3)]$ (**1**) may be described as a Rh^{-I}/Ga^{III} complex, which, according to the synthesis path, is formed by a (formal) oxidative addition of a Rh–CH_3 bond to the Ga^I center of a GaCp* ligand. The subsequent protolytic cleavage of Cp*H from **1** to yield **2** (Scheme 1) can be assigned as redox neutral. If the particular synthesis route is disregarded, the cation $[(Cp^*Ga)_4Rh(GaCH_3)]^+$ as such may be described as a Rh^I/Ga^I complex, which is composed of a neutral, carbenoid $GaCH_3$ two-electron donor ligand coordinated to an unsaturated 16-electron $[(GaCp^*)_4Rh]^+$ ion. In that latter case, all GaR ligands of **2** are regarded as Ga^I species.

Which description should be preferred? An unambiguous distinction between the two alternatives based on structural or spectroscopic features is not straightforward. The Ga–CH_3 bond lengths of 198.9 (12) pm for **1** and 195.8(11) pm for **2** are shorter than the calculated (DFT) bond length of 204.9 pm for matrix-isolated, free (monovalent) $GaCH_3$[5] and are close to the length of the Ga–C bond in (trivalent) $Ga(CH_3)_3$ (196.7(2) pm).[10] This comparison may support the Rh^{-I}/Ga^{III} view. To gain a better insight into the situation, we carried out DFT calculations similar to those reported for $[(Cp^*Ga)_4PtGa]^{+}$[3] (see the Supporting Information). The calculated charge on the gallium atom of the $GaCH_3$ group (1.06) in the model complex $[(CpGa)_4Rh(GaCH_3)]^+$ is higher than that on the GaCp ligands (0.78/0.79), but substantially lower than in the cation $[Ga(CH_3)_2]^{2+}$ (1.70). The charge at the Rh center was calculated to be −0.97. An energy decomposition analysis (EDA)[11] reveals that a fragmentation into $[(CpGa)_4Rh]^+$ and $GaCH_3$ ($\Delta E_{int} = -83.1$ kcal mol^{-1}) requires much less energy than a homolytic cleavage ($\Delta E_{int} = -127.4$ kcal mol^{-1}), whereas the energy needed for the decomposition into $[(CpGa)_4Rh]^-$ and $[GaCH_3]^{2+}$ ($\Delta E_{int} = -457.8$ kcal mol^{-1}) is very high. More than just the calculated charges and EDA results obtained from DFT are required to substantiate a formal assignment of oxidation state.[12] For instance, all Ga atoms in **2** are dicoordinate and trivalent, because they use all three valence electrons for binding to their R group and the Rh center. Furthermore, all Ga atoms are more positively charged than in a free GaR group or in neutral $[M(GaR)_n]$ complexes.[13] The stronger effect at Ga1 compared to the other Ga atoms is caused by the absence of π-electron donation from a Cp* group. Therefore, we prefer the description of **2** as a pseudo-homoleptic Ga^I complex in accordance the synthesis of the cation $[(Cp^*Ga)_5Rh]^+$ and the conventional view of $[L_5Rh]^+$ complexes as Rh^I species. A similar discussion has taken place on the complexes $[M(CO)_n(ECp^*)]$ (M = Fe, Cr; E = Al, Ga; n = 4, 5), for which the Group 13 center has been considered as E^{III} rather than E^I based on the electronegativity of the $\{M(CO)_n\}$ fragment.[14,15] Nevertheless, taking into account complexes such as $[M(CO)_3(GaCp^*)_3]$[16] (M = Mo, W), the whole series of compounds may be better described as E^I complexes.

According to theoretical studies on model compounds such as $[(Cp^*Ga)_4PtGa]^+$,[3] $[M(CO)_n(ER)]$,[13] and the homoleptic series $[M(ER)_n]$,[13c] (Fe, $n = 5$; Ni, $n = 4$) the σ-donor strength of GaCp* (as well $GaRL_2$ with R = CH_3 and L = Lewis base ligand)[13d] is higher than that of Ga^+ and $GaCH_3$, while at the same time the π-acceptor capacity is lower due to overlap of the Cp* π orbitals with the p orbitals of the gallium atom. Strong σ-donation results in a large electrostatic contribution to the overall M–E bond energy[3,13c] and leads to short M–E bonds, if steric repulsion is negligible. The coordination of a Lewis base donor L to the $GaCH_3$ unit should lead to a shortening of the respective M–Ga bond, because the $Ga(CH_3)L$ fragment should be a stronger σ donor than $GaCH_3$.[13c–e]

The reaction of **2** with an equimolar amount of pyridine in Et_2O at room temperature and crystallization of the product by slow diffusion of *n*-hexane led to the formation of large yellow single crystals of $[(Cp^*Ga)_4Rh\{Ga(CH_3)(py)\}]BAr^F_4$ (**3**). A single-crystal X-ray structure analysis[17] proved that the pyridine is coordinated to the $GaCH_3$ moiety, thus forming, similar to the situation in **1,** a $Ga(CH_3)py$ unit (Figure 2). The Ga–N bond length of 212.6(4) pm is well in the range of gallium–pyridine adducts, whereas the $Ga-CH_3$ bond length remains unchanged. As expected, the coordination of pyridine leads to a pronounced shortening of the Rh–Ga1 bond from 247.11(10) pm in **2** to 233.41(6) pm in **3**, such that now all the Rh–Ga bonds are equal within the accuracy of the structural refinement! The fact that the addition of a neutral σ donor to the $GaCH_3$ group leads to a shortening of the Rh–Ga bond clearly shows that the π-backdonation from Rh to the electrophilic $GaCH_3$ ligand in **2** is weak and not preferred. These results substantiate the conclusions drawn from theoretical studies[13] that comparably short M–ER bond lengths do not necessarily simply reflect covalent M–E multiple bond interactions.

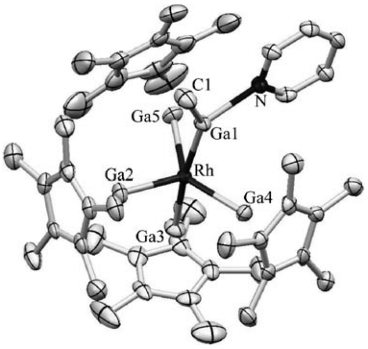

Figure 2. Structure of the cation in **3** (thermal ellipsoids are shown with 50% probability, hydrogen atoms have been omitted for clarity). Selected bond lengths [pm] and angles [°]: Rh-Ga1 233.41(6), Rh-Ga2 234.56(6), Rh-Ga4 233.30(7), Rh-Ga5 233.35(7), Rh-Ga3 236.27(7), Ga1-C1 196.5(5), Ga1-N 212.6(4); Ga1-Rh-Ga3 172.46(3), Ga4-Rh-Ga2 110.85(3), N-Ga1-Rh 117.75(10), C1-Ga1-Rh 143.69(15).

The cation $[(Cp^*Ga)_4Rh(GaCH_3)]^+$ is one of the very rare examples of pseudo-homoleptic complexes with high coordination numbers ($n > 4$) and ligands that bind to the central metal M via metal atoms. However, this is not only interesting from a structural and bonding point of view. The quite remarkable selective cleavage of a Cp* ligand from the gallium center of the $Ga(CH_3)Cp^*$ moiety of **1** by protonation and release of Cp*H rather than CH_4 might be generally applicable within this class of compounds. This points to the unique properties of Cp* groups compared to the other typical substituents R, which are necessary for the stabilization of low-valent Group 13 compounds, in particular the N,N chelating bisketoiminates and related compounds.[1a] The fluxional behavior of Cp* coordinated to main group elements,[18] and the comparably weak bonding of Cp* to the Group 13 centers in particular allows their use as a protecting group, which can be removed under suitable conditions. In this respect our results may be quite relevant for transition-metal Group 13 metal cluster and nanoparticle chemistry.[1d]

Experimental Section

All manipulations were carried out using standard Schlenk line and glove box techniques using dry argon. All solvents were degassed, dried, and saturated with Ar prior to use.

1: $[Rh(CH_3)(cod)(py)]$ (0.3 g, 0.98 mmol) was dissolved in *n*-hexane (5 mL) and treated with six equivalents of GaCp* (1.209 g, 5.90 mmol). Immediately, the color changed from orange to dark red. After the solution was stirred for 30 min at room temperature, the solvent was removed in vacuo and the residue was extracted with isopentane. The solvent volume was reduced to about 3 mL and cooled at −40 °C for 16 h to give the product as a red microcrystalline solid. Crystals suitable for a single-crystal structure analysis were obtained by recrystallization from *n*-hexane. Yield: 0.896 g (89%). ^1H NMR (C_6D_6, 25 °C): $\delta = 1.92$ (75 H, C_5Me_5), 0.34 ppm (3 H, GaMe); ^1H NMR ([D_8]toluene, −100 °C): $\delta = 2.21$ (15 H, η^1-C_5Me_5) 1.93 (60 H, C_5Me_5), −0.05 ppm (3 H, GaMe); ^{13}C NMR (C_6D_6, 25 °C): $\delta = 113.83$ (C_5Me$_5$), 11.75 (C$_5$*Me*$_5$), 10.48 ppm (GaMe). C,H analysis (%) calcd for $C_{51}H_{78}Ga_5Rh$: C 53.61, H 6.88; found: C 53.29, H 6.70.

2: A solution of $[H(OEt_2)_2]BAr^F_4$ (0.443 g, 0.44 mmol) in fluorobenzene (4 mL) was added at −30 °C under rigorous stirring to a solution of **1** (0.500 g, 0.44 mmol) in fluorobenzene (4 mL) by using the canula technique. After the reaction mixture was allowed to warm slowly to room temperature, it was stirred for a further 30 min. The solvent was removed in vacuo and the solid residue was washed with hexane (3 × 3 mL) and dried in vacuo. Single crystals were obtained by slow diffusion of *n*-hexane into a fluorobenzene solution. Yield: 0.638 g (78%). ^1H NMR (fluorobenzene/C_6D_6, 25 °C): $\delta = 8.27$ (8 H, BAr^F_4), 7.56 (4 H, BAr^F_4), 1.64 (60 H, C_5Me_5), 0.54 ppm (3 H, GaMe); ^{13}C NMR (Et_2O/C_6D_6, 25 °C): $\delta = 162.5$ (q, $J = 49.8$ Hz, BAr^F_4), 135.4 (BAr^F_4), 129.8 (q, $J = 31.6$ Hz, BAr^F_4), 125.2 (q, $J = 272.2$ Hz, BAr^F_4), 117.8 (BAr^F_4), 114.7 (C_5Me$_5$), 15.4 (C$_5$*Me*$_5$), 9.8 ppm (GaMe); C,H analysis (%) calcd for $C_{73}H_{75}BF_{24}Ga_5Rh$: C 46.87, H 4.04; found: C 46.37, H 3.65.

3: A sample of **2** (0.200 g, 0.11 mmol) was dissolved in fluorobenzene (4 mL), and pyridine (10 μL g, 0.128 mmol) was added at −30 °C. After the solution was stirred for 30 min at room temperature, all volatiles were removed in vacuo. The pale orange precipitate was redissolved in fluorobenzene (ca. 4 mL) and recrystallized by slow diffusion of *n*-hexane into this solution. Yield: 0.175 g (84%). ^1H NMR ([D_8]THF, 25 °C): $\delta = 8.80$ (3 H, pyridine), 8.19 (2 H, pyridine), 7.80 (8 H, BAr^F_4), 7.58 (4 H, BAr^F_4), 1.86 (60 H, C_5Me_5), 0.70 ppm (3 H, GaMe); ^{13}C NMR ([D_8]THF, 25 °C): $\delta = 163.0$ (q, $J = 49.8$ Hz, BAr^F_4), 149.3 (C_5H_5N), 135.8 (BAr^F_4), 130.2 (q, $J = 28.7$ Hz, BAr^F_4), 127.1 (C_5H_5N), 125.7 (q, $J = 272.2$ Hz, BAr^F_4), 118.4 (BAr^F_4), 115.9 (C_5Me$_5$), 115.4 (C_5H_5N), 10.6 (C$_5$*Me*$_5$), 10.3 ppm (GaMe); C,H,N analysis (%) calcd for $C_{73}H_{75}BF_{24}Ga_5Rh$: C 47.83, H 3.96, N 0.72; found: C 46.99, H 4.04, N 0.98.

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[1] a) H. Braunschweig, K. Radacki, K. Uttinger, *Angew. Chem.* **2007**, *119*, 4054–4057; *Angew. Chem. Int. Ed.* **2007**, *46*, 3979–3982; b) H. Braunschweig, M. Burzler, K. Radacki, F. Seeler, *Angew. Chem.* **2007**, *119*, 7932; *Angew. Chem. Int. Ed.* **2007**, *46*, 7785–7787; c) C. Jones, P. C. Junk, J. A. Platts, A. Stasch, *J. Am. Chem. Soc.* **2006**, *128*, 2206–2207; d) R. J. Baker, C. Jones,

Coord. Chem. Rev. **2005**, *249*, 1857 – 1869; e) N. J. Hardman, R. J. Wright, A. D. Phillips, P. P. Power, *J. Am. Chem. Soc.* **2003**, *125*, 2667 – 2679; f) N. J. Hardman, B. E. Eichler, P. P. Power, *Chem. Commun.* **2000**, 1991 – 1992.

[2] a) T. Cadenbach, C. Gemel, R. Schmid, R. A. Fischer, *J. Am. Chem. Soc.* **2005**, *127*, 17068 – 17078; b) T. Steinke, M. Cokoja, C. Gemel, A. Kempter, A. Krapp, G. Frenking, U. Zenneck, R. A. Fischer. *Angew. Chem.* **2005**, *117, 3003–3007; Angew. Chem. Int. Ed.* **2005**, 44, 2943 – 2946; *Angew. Chem. Int. Ed.* **2005**, *44*, 2943 – 2946; c) T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, *Angew. Chem.* **2004**, *116*, 2349 – 2352; *Angew. Chem. Int. Ed.* **2004**, *43*, 2299 – 2302.

[3] a) B. Buchin, C. Gemel, T. Cadenbach, I. Fernandez, G. Frenking, R. A. Fischer, *Angew. Chem.* **2006**, *118*, 5331 – 5334; *Angew. Chem. Int. Ed.* **2006**, *45*, 5207 – 5210; b) S. Aldridge, *Angew. Chem.* **2006**, *118*, 8275 – 8277; *Angew. Chem. Int. Ed.* **2006**, *45*, 8097 – 8099.

[4] A. Schnepf, H. Schnöckel, *Angew. Chem.* **2002**, *114*, 3682 – 3704; *Angew. Chem. Int. Ed.* **2002**, *41*, 3532 – 3552.

[5] a) H. J. Himmel, A. J. Downs, T. M. Greene, L. Andrews, *Chem. Commun.* **1999**, 2243 – 2244; b) H. J. Himmel, A. J. Downs, T. M. Greene, L. Andrews, *Organometallics* **2000**, *19*, 1060 – 1070.

[6] R. A. Fischer, M. M. Schulte, E. Herdtweck, M. R. Mattner, *Inorg. Chem.* **1997**, *36*, 2010 – 2017.

[7] J. T. Golden, T. H. Peterson, P. L. Holland, R. G. Bergman, R. A. Andersen, *J. Am. Chem. Soc.* **1998**, *120*, 223 – 224.

[8] a) A. Kempter, C. Gemel, N. J. Hardman, R. A. Fischer, *Inorg. Chem.* **2006**, *45*, 3133 – 3138; b) T. Steinke, C. Gemel, M. Cokoja, M. Winter, R. A. Fischer, *Dalton Trans.* **2005**, 55 – 62.

[9] a) Crystal structure analysis of **2**: crystal size: $0.15 \times 0.10 \times 0.10\ \mathrm{mm}^3$, monoclinic, $P2/n$, $a = 15.8518(10)$, $b = 12.8256(8)$, $c = 19.4342(6)$ Å, $\beta = 98.661(4)^\circ$, $V = 3906.1(4)$ Å^3, $Z = 2$, $\rho_{\mathrm{calcd}} = 1.590\ \mathrm{mg\,m^{-3}}$, $2\theta_{\mathrm{max}} = 55.20$, $\lambda(\mathrm{Mo}_{\mathrm{K}\alpha}) = 0.71073$ Å, $T = 113(2)$ K. A total of 39237 reflections (9036 unique) were measured on an Oxford Excalibur 2 diffractometer [$R(\mathrm{int}) = 0.0651$]. The structural solution and refinement was done using the programs SHELXS-97 and SHELXL-97.[19] The final values for $R1$ and $wR2(F^2)$ were 0.0536 and 0.1348 (all data). b) CCDC-670890 (**2**) and CCDC-670891 (**3**) 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.

[10] B. Beagley, D. G. Schmidli, I. A. Steer, *J. Mol. Struct.* **1974**, *21*, 437 – 444.

[11] a) J. Krijn, E. J. Baerends, *Fit Functions in the HFS-Method*, Internal Report, Vrije Universiteit Amsterdam, Niederlande, **1984** (in Dutch). All calculations were performed by using the program package ADF; b) F. M. Bickelhaupt, E. J. Baerends, *Reviews in Computational Chemistry, Vol. 15* (Eds.: K. B. Lipkowitz, D. B. Boyd), Wiley-VCH, New York, **2000**, p. 1; c) G. te Velde, F. M. Bickelhaupt, E. J. Baerends, S. J. A. van Gisbergen, C. Fonseca Guerra, J. G. Snijders, T. Ziegler, *J. Comput. Chem.* **2001**, *22*, 931 – 967. The atomic partial charges were calculated by using the Hirshfeld method: F. L. Hirshfeld, *Theor. Chim. Acta* **1977**, *44*, 129; d) T. Ziegler, A. Rauk, *Theor. Chim. Acta* **1977**, *46*, 1 – 10; e) K. Morokuma, *J. Chem. Phys.* **1971**, *55*, 1236 – 1244. f) The EDA partitions the instantaneous interaction energy between the bonded fragments ΔE_{int} into three main contributions, namely the Pauli repulsion $\Delta E_{\mathrm{Pauli}}$, the quasi-classical electrostatic interaction $\Delta E_{\mathrm{elstat}}$, and the orbital (covalent) interaction ΔE_{orb}. The latter term can be divided into the contributions ΔE_{σ} and ΔE_{π} for orbitals possessing σ and π symmetry.

[12] In this regard, we remind the reader of the valuable article on “valence” and “oxidation numbers”: G. Parkin, *J. Chem. Educ.* **2006**, *83*, 791 – 799.

[13] a) F. A. Cotton, X. J. Feng, *Organometallics* **1998**, *17*, 128 – 130; b) C. Boehme, G. Frenking, *Chem. Eur. J.* **1999**, *5*, 2184 – 2190; c) J. Uddin, C. Boehme, G. Frenking, *Organometallics* **2000**, *19*, 571 – 582; d) R. A. Fischer, M. M. Schulte, J. Weiss, L. Zsolnai, A. Jacobi, G. Huttner, G. Frenking, C. Boehme, S. F. Vyboishchikov, *J. Am. Chem. Soc.* **1998**, *120*, 1237 – 1248; e) C. L. B. Macdonald, A. H. Cowley, *J. Am. Chem. Soc.* **1999**, *121*, 12113 – 12126.

[14] J. Weiß, D. Stetzkamp, B. Nuber, R. A. Fischer, C. Boehme, G. Frenking, *Angew. Chem.* **1997**, *109*, 95 – 97; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 70 – 72.

[15] Q. Yu, A. Purath, A. Donchev, H. Schnöckel, *J. Organomet. Chem.* **1999**, *584*, 94 – 97.

[16] M. Cokoja, T. Steinke, C. Gemel, T. Welzel, M. Winter, K. Merz, R. A. Fischer, *J. Organomet. Chem.* **2003**, *684*, 277 – 286.

[17] Crystal structure analysis of **3**: crystal size: $0.15 \times 0.15 \times 0.10\ \mathrm{mm}^3$, monoclinic, $P2(1)/c$, $a = 20.9830(16)$, $b = 20.522(2)$, $c = 20.064(2)$ Å, $\beta = 107.195(11)^\circ$, $V = 8254.0(14)$ Å^3, $Z = 4$, $\rho_{\mathrm{calcd}} = 1.569\ \mathrm{mg\,m^{-3}}$, $2\theta_{\mathrm{max}} = 55.26$, $\lambda(\mathrm{Mo}_{\mathrm{K}\alpha}) = 0.71073$ Å, $T = 113(2)$ K. A total of 70713 reflections (19130 unique) were measured on an Oxford Excalibur 2 diffractometer [$R(\mathrm{int}) = 0.0740$]. The structural solution and refinement was done using the programs SHELXS-97 and SHELXL-97.[19] The final values for $R1$ and $wR2(F^2)$ were 0.0416 and 0.1048 (all data).[9b]

[18] P. Jutzi, G. Reumann, *J. Chem. Soc. Dalton Trans.* **2000**, 2237 – 2244.

[19] G. M. Sheldrick, SHELXS-97, Program for the Solution of Crystal Structures, Universität Göttingen, **1997**; G. M. Sheldrick, SHELXL-97, Program for Crystal Structure Refinement, Universität Göttingen, **1997**.