NMR Chemical Shifts of Zr@C_{28}. How Shielded Can ^{91}Zr Get?

M. Bühl[†]

Organisch-chemisches Institut, Universität Zürich, Winterthurerstr. 190, CH-8057 Zürich, Switzerland

Received: November 21, 1996; In Final Form: January 24, 1997[⊗]

A ^{91}Zr chemical shift of −1500 ppm (relative to $(C_5H_5)_2ZrBr_2$) is predicted for Zr@C_{28} at the GIAO (gauge-including atomic orbitals)-B3LYP level using a medium-sized basis set and SCF optimized geometries. This value is even more shielded than the one predicted for hypothetical $(\eta^5\text{-}C_5H_5)_4Zr$, ca. −1100 ppm at the same level. A noticeable deshielding with repect to Zr@C_{28} is indicated for Zr@$C_{28}H_2$, a model for exohedrally substituted derivatives. Electron correlation effects on $\delta(^{91}Zr)$, as assessed by GIAO-B3LYP vs GIAO-SCF results, are much larger for these endohedral Zr fullerenes than for any other Zr compound studied so far. According to the computed electric field gradients, quadrupolar line broadening should be large for the known $(\eta^5\text{-}C_5H_5)_3(\eta^1\text{-}C_5H_5)Zr$ but should be small for Zr@$C_{28}H_2$. Since Zr@C_{28} has been detected mass-spectroscopically "in substantial yield" (Guo, T.; et al. *Science* **1992**, *257*, 1661), ^{91}Zr NMR spectroscopy is suggested as the analytical method of choice for Zr@C_{28} and derivatives thereof.

Introduction

The endohedral trapping of atoms or molecules is one of the many fascinating aspects of fullerene chemistry.[1−6] Since the first mass spectroscopic evidence for metallofullerenes as early as 1985,[7] their preparation and characterization are areas of active research.[1−4,6] These compounds usually consist of group III metals (including lanthanides) and larger fullerenes, for example, Y@C_{82},[2] and direct and indirect spectroscopic evidence leave little doubt about their endohedral nature. Compounds of smaller fullerenes have not yet been isolated in macroscopic amounts, but mass spectroscopy has indicated that some species may be remarkably stable, in particular M@C_{28} (M = U, Zr, Hf).[4] These findings have stimulated a number of theoretical studies that have indicated that C_{28} can form four bonds either "to the outside" or "to the inside", affording presumably stable, closed-shell species $C_{28}A_4$ (A = univalent atom) or M@C_{28} (M = tetravalent, electropositive metal), respectively.[8,9]

For endohedral He fullerene compounds, ^{3}He NMR spectroscopy has proven to be a valuable analytical tool.[10,11] Ab initio GIAO (gauge-including atomic orbitals)-SCF computations have satisfactorily reproduced the endohedral chemical shifts of He@C_{60} and He@C_{70}[12,13] and may be useful for assigning the corresponding signals of higher fullerenes.[14] Results of chemical shift calculations for Zr@C_{28} and Zr@$C_{28}H_2$ are now reported that suggest that ^{91}Zr NMR spectroscopy may be similarly well suited for characterization of the zircono-fullerene and for the investigation of its chemistry. Since trends of ^{91}Zr chemical shifts of zirconocenes have been qualitatively reproduced at the SCF level,[15] predicted $\delta(^{91}Zr)$ values of some Zr cyclopentadienyl complexes are also given for comparison. Special attention is called to the effects of electron correlation on the computed chemical shifts as assessed by density functional theory (DFT). DFT-based methods have successfully been applied to chemical shift calculations for ligands in the coordination sphere of transition metals,[16−18] as well as for the transition metal chemical shifts themselves, in particular for $\delta(^{103}Rh)$ and $\delta(^{57}Fe)$.[19]

Methods

The same methods and basis sets as in the study on zirconocenes have been employed.[15] Geometries have been optimized[20] with the TURBOMOLE program[21] at the SCF/B′ level, i.e., employing a relativistic ME-fit effective core potential (ecp) together with a valence [5s5p2d] basis on Zr[22] and standard 6-31G* basis[20] on C and H. The following energies and properties have been evaluated for these geometries. EFGs (electric field gradients) have been computed with the Gaussian suite of programs[23,24] using basis B, i.e., a contracted and augmented [12s11p7d] all-electron basis for Zr,[25,26] a relativistic ME-fit ecp with a valence [2s2p1d] basis for Br,[27−30] and standard 6-31G* basis on all other atoms. Largest absolute values $|q_{zz}|$ are given in atomic units (1 au = 9.7174×10^{21} V m^{-2}). Magnetic shieldings σ have been computed using the GIAO-SCF method[31,32] in its direct versions as implemented in TURBOMOLE[33] and Gaussian 94,[34] together with basis B. In addition, σ values have been computed at gradient-corrected GIAO-DFT levels, employing Becke's 1988 exchange[35] and Perdew's 1986 correlation functionals[36] (denoted GIAO-BP86), as well as Becke's three-parameter DFT/HF hybrid functional for exchange[37] together with the correlation functional by Lee, Yang, and Parr[38] (denoted GIAO-B3LYP) as implemented in Gaussian 94.[34] ^{91}Zr chemical shifts δ are reported relative to the experimental standard, $(C_5H_5)_2ZrBr_2$, with computed σ values of 2502, 1527, and 1679 ppm for GIAO-SCF, GIAO-BP86, and GIAO-B3LYP levels, respectively. ^{13}C chemical shifts have been referenced to benzene (σ = 75.6, 74.1, and 71.6 ppm, respectively, at the same levels) and converted to the usual δ scale using the experimental chemical shift of benzene, 128.5 ppm. In addition, GIAO-SCF computations have been performed using the basis II (essentially polarized triple-ζ quality for the ligands) described earlier.[15]

Singlet−triplet splittings have been evaluated by single-point energy calculations for the triplet state employing the unrestricted Hartree−Fock and DFT formalisms, together with basis B and the optimized singlet-state geometries. These single-point calculations have been performed using the Gaussian 94 program. Unless otherwise noted, energies are reported at the BP86/B//SCF/B′ level (in the usual "level of energy calculation//level of geometry optimization" notation).

[†] Fax: 0041-1-361 9895. E-mail: buehl@oci.unizh.ch.

[⊗] Abstract published in *Advance ACS Abstracts,* March 1, 1997.

S1089-5639(96)03882-0 CCC: $14.00

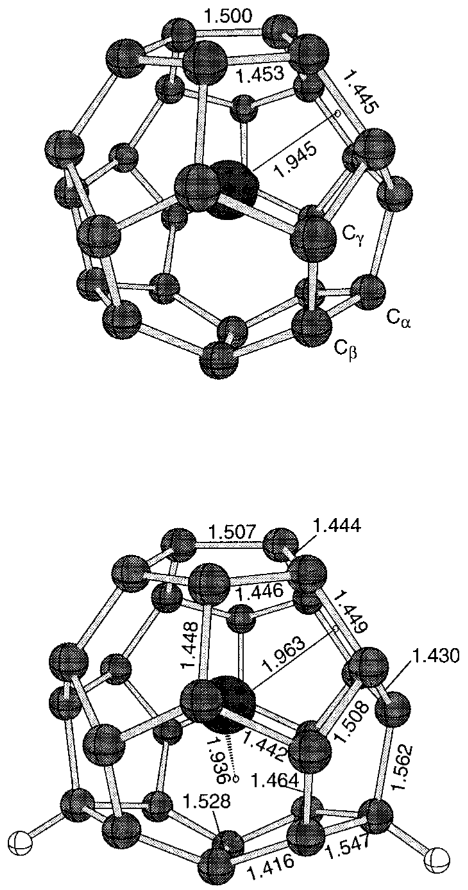

Figure 1. SCF/B′ optimized structure of Zr@C_{28} (T_d, top) and Zr@$C_{28}H_2$ (C_{2v}, bottom). Bond lengths are in angstroms, and the small ○ denotes centers of mass of the six-membered rings.

Results and Discussion

Chemical Shifts. The SCF/B′ optimized geometrical parameters of Zr@C_{28} (Figure 1) are in good agreement with those predicted earlier at a comparable theoretical level.[8] According to the computed chemical shift data in Table 1, the Zr nucleus is strongly shielded in Zr@C_{28}, with $\delta(^{91}Zr)$ between −980 (GIAO-SCF) and −1565 ppm (GIAO-BP86; note the large electron-correlation effect; see below). The ^{91}Zr resonance at the lowest frequency known to date is probably that of $(C_5H_5)_2$-Zr[$N(SO_2CF_3)_2$]/CH_3CN with $\delta(^{91}Zr) = -455$ ppm.[39] Apparently, the paramagnetic contributions to the magnetic shielding, σ_{para}, are much reduced in Zr@C_{28} as compared to other Zr compounds. This decrease of σ_{para} in Zr@C_{28} is consistent with the reported large HOMO−LUMO separation (>8 eV), which has been taken—together with the notable binding energy relative to Zr and C_{28}—as evidence for an "expected stability".[8]

The bonding in η^5-cyclopentadienyl metal complexes shares some of these characteristics, namely, strong binding, large energetic separations of the magnetically active occupied and virtual orbitals, and, consequently, an apparent shielding (or, rather, reduced deshielding) of the central metal atom.[40] To put the Zr@C_{28} results in this context, Zr complexes with three and four η^5-C_5H_5 ligands have been investigated, namely, $(\eta^5$-$C_5H_5)_3(\eta^1$-$C_5H_5)$Zr and $(\eta^5$-$C_5H_5)_4$Zr in C_1 and S_4 symmetry, respectively. The ^{91}Zr chemical shift of hypothetical $(\eta^5$-$C_5H_5)_4$-Zr, between −1036 (GIAO-SCF) and −1091 ppm (GIAO-B3LYP), is also strongly shielded but not as much as in Zr@C_{28}. $(C_5H_5)_4$Zr is known, but only three of the cyclopentadienyl rings are η^5-bonded; the fourth one is bonded in a η^1 fashion.[41] Accordingly, $(\eta^5$-$C_5H_5)_3(\eta^1$-$C_5H_5)$Zr in C_1 symmetry is computed to be much more stable than $(\eta^5$-$C_5H_5)_4$Zr, namely, by 28.4 kcal/mol (BP86/B//SCF/B′ level), and the $\delta(^{91}Zr)$ value of the former is predicted to be less shielded, between −505 (GIAO-SCF) and −640 ppm (GIAO-BP86).

With a predicted $\delta(^{91}Zr)$ value much more negative than that of $(\eta^5$-$C_5H_5)_4$Zr, Zr@C_{28} is probably the compound with the most shielded ^{91}Zr nucleus conceivable and should be readily identified by its ^{91}Zr chemical shift. As with ^{3}He NMR for endohedral He fullerenes,[10,11] ^{91}Zr NMR should be a particularly "clean" analytical tool for Zr@C_{28}; the corresponding ^{13}C NMR spectrum may be complicated by eventual side or decomposition products. The theoretical ^{13}C chemical shifts, which may be helpful in the assignments, are 150.4 (C_α), 150.5 (C_γ), and 177.4 ppm (C_β, carbon positions as indicated in Figure 1) at the GIAO-B3LYP level.[42]

In He fullerene compounds, the endohedral ^{3}He chemical shifts are determined by the ring currents of the fullerene cages.[14,43] Four benzene-like rings can be identified in the Zr@C_{28} structure (with a CC bond length of 1.445 Å; see Figure 1). An estimate for the ring current contributions to the ^{91}Zr shielding may be provided by "exohedrally" saturated $C_{28}H_4$. The computed chemical shift at the center of this molecule is −6 ppm, suggesting that ring current effects are relatively small in Zr@C_{28} (chemical shifts of points in space have been used to study ring current effects in higher fullerenes[14] and have been termed nucleus-independent chemical shifts, NICS[44]).

Electron correlation effects on $\delta(^{91}Zr)$, as assessed by the GIAO-DFT methods, are very large for Zr@C_{28}, more than 500 ppm (compare GIAO-SCF and GIAO-BP86 or -B3LYP values in Table 1), and are also substantial for $(\eta^5$-$C_5H_5)_3(\eta^1$-$C_5H_5)$-Zr, more than 120 ppm. Some zirconocenes, for which experimental trends in $\delta(^{91}Zr)$ have been qualitatively reproduced at the GIAO-SCF level, are included in Table 1. For these species, electron correlation effects vary between ca. 50 and 120 ppm. The GIAO-DFT values offer no improvement over the GIAO-SCF data and appear to be computed consistently too strongly deshielded. Note that the use of a larger basis set on the ligands reduces the $\delta(^{91}Zr)$ values up to ca. 25 ppm at the GIAO-SCF level (see the data in parentheses in Table 1). Even larger basis sets and probably also better geometries may be needed in conjunction with DFT-based methods for an improved description of ^{91}Zr chemical shifts. It thus appears that the relatively good performance of the GIAO-SCF method may be fortuitous to some extent. Nevertheless, the qualitative trends are very similar at all levels employed, and the GIAO-DFT values predicted for Zr@C_{28}, −1565 (GIAO-BP86) and −1500 ppm (GIAO-B3LYP), should be in the right order of magnitude.

Zr@C_{28} Derivatives. C_{28} has been described as "a hollow superatom" with with four unpaired electrons capable of forming four bonds either to the inside or to the outside.[4,8] If C_{28} could be synthesized in macroscopic amounts, it would most likely polymerize instantly by intermolecular combination of the "dangling" bonds. Compounds such as Zr@C_{28}, on the other hand, are closed-shell species, electronically saturated, and possibly quite stable. Conversion of endohedral to exohedral bonds may constitute an important aspect of their as yet unknown chemistry. To study the effect on the magnetic properties of such a "bond conversion", Zr@$C_{28}H_2$ has been investigated. The C_{2v} optimized structure is included in Figure 1. Geometrical changes with respect to Zr@C_{28} are concentrated on the CC bond lengths involving the H-bearing carbons.

According to UHF single-point calculations, triplet Zr@$C_{28}H_2$ is more stable than the singlet state by 0.3 eV and shows a significant contamination of higher spin states (the expectation value of the total spin operator, $\langle \hat{S}^2 \rangle$, is ca. 3 instead of 2 as

TABLE 1: Theoretical ^{91}Zr Chemical Shifts of Zirconofullerenes and Cyclopentadienyl Zr Complexes, Employing Basis B and SCF/B′ and GIAO-SCF/II Geometries

		$\delta(^{91}\mathrm{Zr})^a$				
compound	symmetry	GIAO-SCF	GIAO-SCF/II	-BP86	-B3LYP	expt^b
$\mathrm{Zr@C_{28}}$	T_d	−979	−980	−1565	−1500	
$\mathrm{Zr@C_{28}H_2}$	C_{2v}	−677	−688	−1287	−1193	
$(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{Zr}$	S_4	−1039	−1036	−1051	−1091	
$(\eta^5\text{-}\mathrm{C_5H_5})_3(\eta^1\text{-}\mathrm{C_5H_5})\mathrm{Zr}$	C_1	−505	−515	−640	−626	
$\mathrm{(C_5H_5)_2ZrCl_2}$	C_2	−62	−85^c	−100	−104	−112
$\mathrm{(C_5Me_5)_2ZrCl_2}$	C_s	50	28^c	170	138	85
$\mathrm{(C_5H_5)_2ZrMe_2}$	C_{2v}	430	406^c	483	460	386

[a] In ppm relative to $\mathrm{(C_5H_5)_2ZrBr_2}$. [c] From ref 15.

expected for a pure triplet). At the unrestricted BP86 level, spin contamination is negligible and the triplet is predicted to be 1.1 eV above the singlet ground state. It is likely that higher theoretical levels, in particular those based on multiconfigurational approaches, might be needed for definite conclusions regarding the electronic states of $\mathrm{Zr@C_{28}H_2}$. The same may be true for $\mathrm{Zr@C_{28}}$, where the computed singlet−triplet gap, 3.3 eV at the UHF level (also heavily spin-contaminated; $\langle \hat{S}^2 \rangle \approx 2.5$), is reduced to 2.2 eV at UBP86. For $\mathrm{Hf@C_{28}}$, in contrast, electron correlation at the CISD level has been reported to increase the separation between the singlet ground state and the lowest triplet state.[9]

According to the rather preliminary results presented here, $\mathrm{Zr@C_{28}}$ may be quite reactive and derivatization may proceed easily. For instance, the hydrogenation reaction

$$\mathrm{Zr@C_{28} + H_2 \rightarrow Zr@C_{28}H_2}$$

is computed to be exothermic by −24.7 kcal/mol at the BP86/B//SCF/B′ level (SCF level gives −11.4 kcal/mol).

From the smaller energetic difference of occupied and virtual MOs in $\mathrm{Zr@C_{28}H_2}$ with respect to $\mathrm{Zr@C_{28}}$, an increase in σ_para is to be expected for the former. Indeed, the Zr atom in $\mathrm{Zr@C_{28}H_2}$ is computed to be deshielded with respect to that in $\mathrm{Zr@C_{28}}$ by ca. 300 ppm (GIAO-SCF and -B3LYP levels; see Table 1). Thus, ^{91}Zr NMR should be a sensitive probe for effects of substituents at the $\mathrm{Zr@C_{28}}$ unit.

Line Widths. Quadrupolar line broadening can be a serious obstacle for ^{91}Zr NMR spectroscopy because in unfavorable cases, the signals can become undetectably broad. In accord with the theory of quadrupolar relaxation,[45] trends in ^{91}Zr NMR line widths $\Delta\nu_{1/2}$ have been rationalized in terms of computed EFGs (or, rather, the square of the largest EFG tensor component, $q_{zz}{}^2$) and experimental correlation times τ_c.[15] For $\mathrm{Zr@C_{28}}$ in point group T_d, the EFG at the Zr atom is zero by symmetry, and a relatively sharp ^{91}Zr NMR resonance may be expected. To estimate the magnitude of quadrupolar line broadening for substituted derivatives, the EFG has been computed for $\mathrm{Zr@C_{28}H_2}$ and is compared to the corresponding data for Zr cyclopentadienyl complexes in Table 2.

As has been noted earlier, the relative trend in the $q_{zz}{}^2$ values in the $\mathrm{(C_5H_5)_2ZrX_2}$ series (X = Br, Cl, Me) parallels the trend in the experimental line widths (between ca. 20 and 2500 Hz).[15] For the $(\eta^5\text{-}\mathrm{C_5H_5})_3\mathrm{Zr}$ species, the computed q_{zz} value is comparable to that of $\mathrm{(C_5H_5)_2ZrMe_2}$; i.e., quadrupolar line broadening should be substantial. Indeed, in the first chemical ^{91}Zr NMR study, the ^{91}Zr resonance of $\mathrm{(C_5H_5)_4Zr}$ has been found to be “so broad as to escape detection”.[46] Apparently, the larger size of this molecule increases τ_c and, consequently, $\Delta\nu_{1/2}$ with respect to those of $\mathrm{(C_5H_5)_2ZrMe_2}$. For substituted $\mathrm{Zr@C_{28}}$ derivatives, even larger τ_c values are to be expected. If a large EFG at the endohedral Zr atom would add to the line broadening, it is unlikely that the ^{91}Zr resonance could be detected. However, the computed q_{zz} value for $\mathrm{Zr@C_{28}H_2}$ is quite small (Table 2),[47] smaller even than that of $\mathrm{(C_5H_5)_2ZrBr_2}$, the compound with the narrowest line so far. Thus, ^{91}Zr NMR signals of $\mathrm{Zr@C_{28}}$ derivatives should be recordable, provided the substituents are not so bulky as to increase τ_c excessively.

TABLE 2: Computed (SCF/B//SCF/B′) Absolute and Relative EFGs of Cyclopentadienyl Zr Complexes and of $\mathbf{Zr@C_{28}H_2}$, Together with Relative Line Widths of Zirconocenes

compound	$\lvert q_{zz}\rvert^a$	$q_{zz}{}^2(\mathrm{rel})^b$	$\Delta\nu_{1/2}(\mathrm{rel})^{b,c}$
$\mathrm{(C_5H_5)_2ZrBr_2}^c$	0.155	0.3	0.1
$\mathrm{(C_5H_5)_2ZrCl_2}^c$	0.299	1	1
$\mathrm{(C_5H_5)_2ZrMe_2}^c$	0.935	9.7	9.4
$(\eta^5\text{-}\mathrm{C_5H_5})_3(\eta^1\text{-}\mathrm{C_5H_5})\mathrm{Zr}$	0.917	9.4	
$\mathrm{Zr@C_{28}H_2}$	0.141	0.2	

[a] In atomic units. [b] Relative to the data for $\mathrm{(C_5H_5)_2ZrCl_2}$. [c] For the experimental $\Delta\nu_{1/2}$ data see ref 15. The EFGs reported there have been obtained for experimental rather than for optimized geometries.

Conclusions

$\mathrm{Zr@C_{28}}$, which has been detected mass spectroscopically, should be readily identified by its ^{91}Zr chemical shift. The predicted $\delta(^{91}\mathrm{Zr})$ value, −1500 ppm at the GIAO-B3LYP level, is strongly shielded, even more so than the ^{91}Zr resonance in hypothetical $(\eta^5\text{-}\mathrm{C_5H_5})_4\mathrm{Zr}$, ca. −1040 ppm at the same level. The electronic structure of $\mathrm{Zr@C_{28}H_2}$, a model for $\mathrm{Zr@C_{28}}$ derivatives, is complicated; a singlet ground state is inferred at a gradient-corrected DFT level, but the computed singlet−triplet gap is small, 1.1 eV. Both GIAO-SCF and GIAO-DFT results indicate a notable deshielding of the Zr atom in $\mathrm{Zr@C_{28}H_2}$ with respect to that in $\mathrm{Zr@C_{28}}$. Quadrupolar line broadening should be small for $\mathrm{Zr@C_{28}H_2}$ as assessed by the computed EFGs. Thus, derivatives of $\mathrm{Zr@C_{28}}$ should also be amenable to identification and investigation by ^{91}Zr NMR spectroscopy.

Acknowledgment. The author thanks Professor Dr. W. Thiel for continuing support. The calculations have been carried out on IBM RS6000 workstations at the university and at ETH Zürich (C4 cluster), as well as on the NEC-SX3 at the CSCS in Manno, Switzerland.

References and Notes

(1) For review, see the following. Bethune, D. S.; Johnson, R. D.; Salem, J. R.; deVries, M. S.; Yannoni, C. S. *Nature* **1993**, *366*, 123.

(2) Takata, M. S.; Umeda, B.; Nishibori, E.; Sakata, M.; Saito, Y.; Ohno, M.; Shinohara, H. *Nature* **1995**, *377*, 46.

(3) Suzuki, T.; Marayuma, Y.; Kato, T.; Kikuchi, K.; Nakao, Y.; Achiba, Y.; Kobayashi, K.; Nagase, S. *Angew. Chem.* **1995**, *107*, 1228.

(4) Guo, T.; Diener, M. D.; Chai, Y.; Alford, M. J.; Haufler, R. E.; McClure, S. M.; Ohno, T.; Weaver, J. H.; Scuseria, G. E.; Smalley, R. E. *Science* **1992**, *257*, 166.

(5) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczowski, S.; Cross, M. L.; Giblin, D. E.; Poreda, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 2193.

(6) Miyake, Y.; Suzuki, S.; Kojima, Y.; Kikuchi, K.; Kobayashi, K.; Nagase, S.; Kainosho, M.; Achiba, Y. *J. Phys. Chem.* **1996**, *100*, 9579.

(7) Heath, J. R.; O'Brien, S. C.; Zhang, Q.; Liu, Y.; Curl, R. F.; Kroto, H. W.; Tittel, F. K.; Smalley, R. E. *J. Am. Chem. Soc.* **1985**, *107*, 7779.

(8) Guo, T.; Smalley, R. E.; Scuseria, G. E. *J. Chem. Phys.* **1993**, *99*, 352.

(9) See the following for examples. Tuan, D. F.; Pitzer, R. M. *J. Phys. Chem.* **1995**, *99*, 9762; *Ibid.* **1995**, *99*, 15069, and extensive bibliography therein.

(10) Saunders, M.; Jiménez-Vázquez, H. A.; Cross, R. J.; Mroczkowski, S.; Freedberg, D. I.; Anet, F. A. L. *Nature* **1994**, *367*, 256.

(11) For review, see the following. Saunders, M.; Cross, R. J.; Jiménez-Vázquez, H. A.; Shimshi, R.; Khong, A. *Science* **1996**, *271*, 1693.

(12) Cioslowski, J. *J. Am. Chem. Soc.* **1994**, *116*, 3619.

(13) Bühl, M.; Thiel, W.; Jiao, H.; Schleyer, P. v. R.; Saunders, M.; Anet, F. A. L. *J. Am. Chem. Soc.* **1994**, *116*, 6005.

(14) Bühl, M.; Wüllen, C. v. *Chem. Phys. Lett.* **1995**, *247*, 63.

(15) Bühl, M.; Hopp, G.; Philipsborn, W. v.; Beck, S.; Prosenc, M. H.; Rief, U.; Brintzinger, H.-H. *Organometallics* **1996**, *15*, 778.

(16) Kaupp, M.; Malkin, V. G.; Malkina, O. L.; Salahub, D. R. *J. Am. Chem. Soc.* **1995**, *117*, 1851.

(17) Kaupp, M. *Chem.—Eur. J.* **1996**, *2*, 194.

(18) Ruiz-Morales, Y.; Schreckenbach, G.; Ziegler, T. *J. Phys. Chem.* **1996**, *100*, 3359.

(19) Bühl, M. *Chem. Phys. Lett.*, in press.

(20) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab initio Molecular Orbital Theory*; Wiley: New York, 1986.

(21) Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, *162*, 165.

(22) Andrae, D.; Häussermann, U.; Dolg, M.; Stoll, H.; Preuss, H. *Theor. Chim. Acta* **1990**, *77*, 123.

(23) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Wong, M. W.; Foresman, J. B.; Robb, M. A.; Head-Gordon, M.; Replogle, E. S.; Gomperts, R.; Andres, L.; Raghavachari, K.; Binkley, J. S.; Gonzales, C.; Martin, R. L.; Fox, D. J.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Pople, J. A. *Gaussian 92/dft*; Gaussian, Inc.: Pittsburgh, PA, 1993.

(24) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; DeFrees, D. J.; Baker, J.; Stewart, J. J. P.; Head-Gordon, M.; Gonzales, C.; Pople, J. A. *Gaussian 94*; Gaussian, Inc.: Pittsburgh, PA, 1995.

(25) Horn, H. Unpublished results.

(26) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571.

(27) Dolg, M.; Wedig, U.; Stoll, H.; Preuss, H. *J. Chem. Phys.* **1987**, *86*, 866.

(28) Dolg, M. Ph.D. Thesis, University of Stuttgart, 1989.

(29) Schwerdtfeger, P.; Dolg, M.; Schwarz, W. H. E.; Bowmaker, G. A.; Boyd, P. D. W. *J. Chem. Phys.* **1989**, *91*, 1762.

(30) Kaupp, M.; Schleyer, P. v. R.; Stoll, H.; Preuss, H. *J. Am. Chem. Soc.* **1991**, *113*, 6012.

(31) Ditchfield, R. *Mol. Phys.* **1974**, *27*, 789.

(32) Wolinski, K.; Hinton, J. F.; Pulay, P. *J. Am. Chem. Soc.* **1990**, *112*, 8251.

(33) Häser, M.; Ahlrichs, R.; Baron, H. P.; Weis, P.; Horn, H. *Theor. Chim. Acta* **1992**, *83*, 455.

(34) Cheeseman, J. R.; Trucks, G. W.; Keith, T. A.; Frisch, M. J. *J. Chem. Phys.* **1996**, *104*, 5497.

(35) Becke, A. D. *Phys. Rev. A* **1988**, *38*, 3098.

(36) Perdew, J. P. *Phys. Rev. B* **1986**, *33*, 8822; *Ibid.* **1996**, *34*, 7406.

(37) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648.

(38) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

(39) Siedle, A. R.; Newmark, R. A.; Gleason, W. B.; Lamanna, W. M. *Organometallics* **1990**, *9*, 1290.

(40) See the following, for example. Ahlrichs, R.; Dohmeier, C.; Gauss, J.; Schneider, U.; Schnöckel, H. *J. Am. Chem. Soc.* **1993**, *115*, 2402.

(41) Rogers, R. D.; Bynum, R. V.; Atwood, J. L. *J. Am. Chem. Soc.* **1978**, *100*, 5238.

(42) The GIAO-BP86 data are similar; GIAO-SCF values are 144.9, 150.5, and 185.6 ppm, respectively.

(43) Haddon, R. C.; Pasquarello, A. *Phys. Rev. B* **1994**, *50*, 16459.

(44) Schleyer, P. v. R.; Maerker, C.; Dransfeld, A.; Jiao, H.; Hommes, N. J. R. v. E. *J. Am. Chem. Soc.* **1996**, *118*, 6317.

(45) Abragam, A. *The Principles of Nuclear Magnetism*; Clarendon Press: Oxford, 1961; p 314.

(46) Sayer, B. G.; Hao, N.; Denes, G.; Bickley, D. G.; McGlinchey, M. J. *Inorg. Chim. Acta* **1981**, *48*, 53.

(47) For Zr@$C_{28}H_2$ the reliability of the SCF value in Table 2 might be questionable because of the triplet instability of the SCF wave function (see text). A similarly small q_{zz} value, however, is obtained at the BP86/B level.