

Pseudopotential Calculations for Methyl Compounds of Zinc and Magnesium

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Pseudopotentials and valence basis sets to be used in calculations for organometallic compounds of zinc and magnesium have been tested in calculations for the $M(\text{CH}_3)_n$ ($M = \text{Zn}, \text{Mg}; n = 1, 2$) molecules. Valence correlation effects are treated at the SDCl and CEPA levels. The capability of a polarization potential on zinc to account for the valence shell contracting effect of core valence correlation is studied. Properties considered are geometries, force constants, Mulliken populations, ionization potentials, atomization, and binding energies. Differences in bonding between the two dimethyl compounds are discussed.

INTRODUCTION

Considering the fact that organozinc and organomagnesium compounds belong to the most important organometallic compounds in synthesis and that zinc and magnesium are of crucial importance also in many biological systems, it is surprising that reliable *ab initio* data on these compounds are very scarce.

Comparing the chemistry of zinc and magnesium is a very rewarding field, because in spite of striking similarities (e.g., atomic and ionic radii, aqueous chemistry) the presence of a filled 3*d*-shell in the zinc atom leads to significant differences (e.g., lower reactivity of the Zn organometallic compounds). The difference of the simple dialkyl compounds is particularly apparent. Dimethyl and diethylzinc, which were already discovered in 1848 by Frankland (cf. reference 1), are volatile liquids that consist of monomers with CZnC-angles of 180°² whereas their magnesium analogues are polymeric solids with bent CMgC-units³ (comparable to the dialkylberyllium compounds) that did not receive much attention in the shadow of the famous Grignard reagents.

For our intended calculations on relatively large complexes of dialkylzinc and dialkylmagnesium compounds with unsaturated nitrogen ligands⁴ we had to choose a practicable *ab initio* approach. The use of pseudopotentials on the metals and for the larger systems even on the first-row elements offers obvious benefits. The question remaining was how large the cores on the metals can be chosen and to what extent the valence basis sets can be truncated without introducing significant errors. Furthermore, be-

cause correlation effects can hardly be treated accurately in larger systems, one should at least be able to estimate, from calculations on smaller molecules, errors which are to be expected at the Hartree-Fock level of theory.

Therefore we have chosen the dimethyl compounds and the methyl radicals of zinc and magnesium to compare results of pseudopotential calculations with different cores (for $M = \text{Zn}$) or pseudopotential and all-electron results (for $M = \text{Mg}$) as well as different basis sets and methods to account for correlation effects; this comparison is made for various properties like geometries, force constants, Mulliken populations, and the energies of ionization, atomization and binding.

While model potential^{5a} and all-electron calculations for Zn(CH₃)₂ (in a paper by Barandiaran et al. on basis sets for studies of transition metal compounds^{5b} and in a comparison of calculated and experimental geometries by Almendinger et al.²) and for MgCH₃ and HMgCH₃⁶ have been done before, the only available comparison of the two dimethyl compounds are single point pseudopotential calculations by Ratner et al.⁷

METHODS

Pseudopotentials

The pseudopotentials $V(r)$ employed are semi-local potentials of the form

$$V(r) = -\frac{Q}{r} + \sum_{l=0}^{l_{\max}} \sum_{i=1}^n C_{li} \exp(-c_{li}r^2) \cdot P_l \quad (1)$$

$$P_l = \sum_{m=-l}^l |Y_{l,m}\rangle \langle Y_{l,m}| \quad (2)$$

where Q is the core charge and P_l is the projector

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on angular momentum l . For zinc the two pseudopotentials compared are a pseudopotential with a Ne-like core⁸ adjusted in an atomic multielectron fit (MEFIT)⁹ to relativistic Dirac-Fock energies and a pseudopotential with an Ar[3 d^{10}]-core¹⁰ fitted with MEFIT to quasirelativistic energies (the parameters of this pseudopotential are listed in the appendix).

For the simulation of core valence correlation effects in conjunction with the latter pseudopotential a semiempirical polarization potential V_{Pol} of the form

$$V_{\text{Pol}} = -\frac{1}{2} \alpha_D (\mathbf{f}(g^{-1}\mathbf{r}))^2 \quad (3)$$

$$g(r) = (1 - \exp(-\delta r^2))^{1/2} \quad (4)$$

is used, where \mathbf{f} is the field generated by valence electrons and surrounding cores at the site of a given core, α_D is the core dipole polarizability and δ is a cutoff parameter.¹¹

Single-electron-fit (SEFIT) pseudopotentials adjusted to experimental and Dirac-Fock data with a Ne-like core for magnesium and with a He-like core for carbon, are taken from references 12 and 13, respectively. In some cases for these two elements all electrons are treated explicitly.

Basis Sets

Generally Gaussian type orbitals (GTO) are employed. For the Ne-core pseudopotential on zinc the optimized (8 $s7p6d$)/[6 $s5p3d$] basis set published with the potential⁸ is used. For some calculations including valence correlation one set of f functions ($\alpha = 0.28$) has been added to enable angular correlation of the d orbitals.

For all-electron calculations on the magnesium compounds the (12 $s9p$)/[6 $s4p$] basis set of McLean and Chandler¹⁴ has been employed which for some correlation calculations is augmented by one set of d -functions ($\alpha = 0.11$).

For the two-valence-electron pseudopotentials on the metals (4 $s2p$)/[3 $s2p$] and (3 $s1p$)/[2 $s1p$] basis sets have been optimized (see appendix).

For carbon in the all-electron case the (9 $s5p1d$)/[3 $s2p1d$] basis set of Dunning and Hay¹⁵ is used. The (4 $s1p$)/[3 $s1p$] and (4 s)/[3 s] basis sets for hydrogen are taken from the same article.

Two basis sets (4 $s4p$)/[2 $s2p$] and (3 $s3p$)/[2 $s2p$] optimized for the pseudopotential on carbon and a (3 s)/[2 s] basis set for hydrogen have also been generated (see appendix).

The combinations of these basis sets as shown in Table I reveal the following pattern: The combinations B1 with Ne-like core and a relatively large basis set on zinc and relatively large all-electron basis sets on magnesium and carbon serve as reference calculations (B1+ denotes calculations with additional f and d functions on Zn

and Mg, respectively). The sets B2 introduce the two-valence electron pseudopotentials with still relatively flexible basis sets on the metals.

The pseudopotential on carbon with a (4 $s4p1d$)/[2 $s2p1d$] basis set (the exponent of the d function is taken from reference 15) is introduced in combination B3. The polarization functions on carbon and hydrogen are removed in B4, while B5 reduces the basis sets on the metals to (3 $s1p$)/[2 $s1p$] as well as the number of primitive functions on carbon and hydrogen.

Methods to Account for Electron Correlation

Valence correlation is included in our calculations by a singles + doubles CI with Davidson's correction¹⁷ added (SDCI+Q), or using the coupled-electron pair approximation¹⁸ (CEPA 1). The programs employed for these calculations are MELD¹⁹ and MOLPRO,^{18,20} respectively. The results of SDCI+Q- and CEPA 1-calculations have been found to be very similar for the $M\text{Me}_2$ ($M = \text{Zn, Mg}$) molecules, so both schemes are used throughout this article.

The magnitude of the correlation energy calculated strongly changes, of course, with the size of the pseudopotential core employed or when explicitly excluding core orbitals from correlation.

Table II shows that for zinc there is a significant contribution from the d shell to the correlation energy, almost half of it originating from angular correlation.

RESULTS AND DISCUSSION

Dimethyl Compounds

Geometries

The barrier of rotation around the MC bonds was found to be negligible in our calculations for both $M = \text{Zn}$ and $M = \text{Mg}$ (which is consistent with the experimental data on dimethylzinc²¹). In subsequent calculations, we chose an eclipsed conformation for geometries close to the energy minimum. Both molecules were generally found to have CMC -angles of 180° in their ground state. The optimized geometries are summarized in Tables III and IV.

At the Hartree-Fock level all pseudopotential/basis set combinations (B1 through B5) used for dimethylzinc give geometries in good agreement with the all-electron SCF calculations of Almenningen et al.² but they overestimate the experimental ZnC-distance by ca. 5 pm. This is consistent with results of Barandiaran et al.^{5b} which show that while minimal basis sets or basis sets with a small inner-core part under-

Table I. Different basis set combinations employed.

	B1	B2	B3	B4	B5
Zn					
Core size	Ne ^a	Ar[3d ¹⁰] ^b	Ar[3d ¹⁰] ^b	Ar[3d ¹⁰] ^b	Ar[3d ¹⁰] ^b
Fit ^c	MDF ^c	MWB ^c	MWB ^c	MWB ^c	MWB ^c
Primitives	8s7p6d ^a	4s2p ^d	4s2p ^d	4s2p ^d	3s1p ^d
Contr. scheme	[511111/22111/411]	[211/11]	[211/11]	[211/11]	[21/1]
Mg					
Core size	—	Ne ^e	Ne ^e	Ne ^e	Ne ^e
Fit ^c	—	SDF ^c	SDF ^c	SDF ^c	SDF ^c
Primitives	12s9p ^f	4s2p ^d	4s2p ^d	4s2p ^d	3s1p ^d
Contr. scheme	[631111/6111]	[211/11]	[211/11]	[211/11]	[21/1]
C					
Core size	—	—	He ^h	He ^h	He ^h
Fit ^c	—	—	SDF ^c	SDF ^c	SDF ^c
Primitives	9s5p1d ^g	9s5p1d ^g	4s4p1d ^d	4s4p ^d	3s3p ^d
Contr. scheme	[721/41/1]	[721/41/1]	[31/31/1]	[31/31]	[21/21]
H					
Primitives	4s1p ^g	4s1p ^g	4s1p ^g	4s ^g	3s ^d
Contr. scheme	[31/1]	[31/1]	[31/1]	[31]	[21]

^aM. Dolg et al.⁸. ^bM. Dolg¹⁰ (see appendix). ^cShorthand notations for the fitting procedures: MWB = MEFIT to quasirelativistic Wood-Boring¹⁶ energies, MDF, SDF = MEFIT or SEFIT, respectively, to Dirac-Fock energies. ^dSee appendix. ^eP. Fuentealba et al.¹². ^fA. D. McLean et al.¹⁴. ^gT. H. Dunning et al.¹⁵. ^hG. Igel-Mann et al.¹³.

Table II. Correlation energies of the dimethyl compounds.

Dimethylzinc			Dimethylmagnesium		
Method	Excl. Orb. ^a	E_{Corr} [a.u.]	Method	Excl. orb. ^a	E_{Corr} [a.u.]
B1+/CEPA 1	Zn3s, 3p; C1s	-0.65260	B1+/CEPA 1	Mg1s, C1s	-0.39820
B1+/SDCI+Q	Zn3s, 3p; C1s	-0.66700	B1/CEPA 1	Mg1s, C1s	-0.39124
B1/CEPA 1	Zn3s, 3p; C1s	-0.53984	B1/CEPA 1	Mg1s, 2s, 2p, C1s	-0.36436
B1/CEPA 1	Zn3s, 3p, 3d; C1s	-0.36017	B2/CEPA 1	C1s	-0.36346
B2/CEPA 1	C1s	-0.36381	B3/CEPA 1		-0.36500
B3/V _{Pol} /SDCI+Q		-0.35969 ^b	B3/SDCI+Q		-0.36116
B3/CEPA 1		-0.36632			

^aOnly the main AO-components of the MOs *explicitly* excluded from correlation are denoted.

^bOnly the valence correlation energy is specified.

Table III. Geometries and MC-force constants of dimethylzinc.

	$R-\text{ZnC}$ [pm]	$\angle\text{ZnCH}$	$R-\text{CH}$ [pm]	$k(\text{ZnC})$ [a.u.] ^a
Experiment ^b	193.0	112.5	—	—
Alleg. calc. ^b	197.7	111.5	—	—
B1	197.7	111.4	109.5	0.286
B2	198.5	111.5	109.5	0.277
B3	198.0	111.6	109.0	0.258
B4	197.9	111.2	109.2	0.264
B5	198.2	111.2	108.7	0.264
B1+/CEPA 1	194.0	111.4	110.5	0.291
B1/CEPA 1 ^c	201.1 ^d	—	—	0.242
B2/CEPA 1	199.0 ^d	—	—	0.240
B3/V _{Pol} /SDCI+Q	194.0	111.4	109.4	0.274
B3/CEPA 1	198.4 ^d	—	—	0.235

^aOnly the force constant of the isolated ZnC stretch was calculated from a third order polynomial.

^bAlmendingen et al.².

^cAll MOs with mainly *d*-orbital-character on zinc have been excluded from correlation.

^dOnly the ZnC-distance has been optimized, starting from the corresponding SCF-geometry.

Table IV. Geometries and MC-force constants of dimethylmagnesium.

	$R - \text{MgC}$ [pm]	$\langle \text{MgCH} \rangle$	$R - \text{CH}$ [pm]	$k(\text{MgC})$ [a.u.] ^a
Experiment	224 ^b	—	—	—
B1	211.0	112.3	109.8	0.215
B2	210.0	112.2	109.8	0.214
B3	210.9	112.1	109.4	0.208
B4	209.5	111.9	109.4	0.215
B5	209.0	111.7	108.8	0.216
B1+/CEPA 1	210.8	111.4	110.7	0.206
B3/SDCI + Q	210.1 ^c	—	—	0.196

^aOnly the force constant of the isolated MgC stretch was calculated from a third-order polynomial.

^bThe experimental value was taken from the polymeric solid (Weiß [3]) where the interatomic distances are probably much longer than for the unknown gas phase structure.

^cOnly the MgC-distance was optimized, starting from the corresponding SCF-geometry

estimate the ZnC-distance larger basis sets overestimate it.

The deviation from experiment can only be reduced by considering both valence and core valence correlation. Neglect of the latter leads to even larger ZnC-distances than the SCF values and consequently yields too small ZnC force constants. The polarization potential together with an SDCI+Q calculation to account for valence correlation significantly improves the ZnC distance and force constant compared to the calculation with valence correlation only.

For dimethylmagnesium the experimental MC-distance taken from the polymeric solid state structure^{3a} is not a good criterion. Taking our best calculation (with B1+/CEPA 1) as a reference (there are no calculations or gas phase data available in the literature), the results suggest that the role of correlation for geometry is only minor; the differences between the various basis sets are below 2 pm and 1° in distances and angles, respectively. The SCF calculations give the usual 10 to 20% overestimate of the MC force constant.

Ionization Potentials

In view of the experimental value of 9.46 eV for dimethylzinc,²² Koopmans' theorem seems to hold

well for this compound whereas the ΔSCF -values consistently are too small by about 0.8 to 0.9 eV (Table V). With B1+/CEPA 1 the major part of the correlation contribution is recovered whereas B3/CEPA 1 yields a much too small contribution. Obviously core valence correlation plays an important role for the first ionization energy in dimethylzinc. Unfortunately the polarization potential does not reproduce this effect.

For dimethylmagnesium no experimental data are available. Comparison with the CEPA 1 calculations suggests, however, that the ΔSCF values are to be preferred here over Koopmans energies.

Energies of Atomization

The calculated values of atomization energies are listed in Table VI. In addition to the uncorrected values, i.e. values obtained by subtracting from the molecular energies the sum of atomic energies evaluated with the corresponding atomic basis sets, we give values corrected for basis set superposition errors (BSSE) where the atomic energies are evaluated with the molecular basis.²³

Generally B1 to B3 show comparable accuracy while B4 shows the effect of the missing polarization functions on carbon and hydrogen. For B5 the BSSE becomes significant, leading to higher uncorrected values than for B4.

Table V. First ionization potentials of the dimethyl compounds [eV].

Dimethylzinc			Dimethylmagnesium		
	Koopmans	ΔSCF		Koopmans	ΔSCF
B1	9.71	8.78	B1	9.30	8.44
B2	9.51	8.62	B2	9.27	8.57
B3	9.45	8.56	B3	9.20	8.52
B4	9.49	8.63	B4	9.23	8.58
B5	9.36	8.59	B5	9.15	8.54
		$\Delta\text{CEPA 1}$			$\Delta\text{CEPA 1}$
B1+/CEPA 1		9.23	B1+/CEPA 1		8.45
B3/V _{Pol} /SDCI + Q		8.77	B1/CEPA 1		8.52
B3/CEPA 1		8.76	B3/CEPA 1		8.45

Table VI. Energies of atomization for the dimethyl compounds [a.u.].

	<i>Dimethylzinc</i>		<i>Dimethylmagnesium</i>		
	Uncorrected ^a	Corrected ^a	Uncorrected ^a	Corrected ^a	
B1	0.844873	0.843728	B1	0.841705	0.840906
B2	0.833401	0.832689	B2	0.842226	0.841350
B3	0.838604	0.837327	B3	0.846865	0.845415
B4	0.803797	0.802563	B4	0.812660	0.811444
B5	0.811695	0.799141	B5	0.824176	0.811368
B1+/CEPA 1	1.040717	1.020426	B1+/CEPA 1	1.034342	
B3/CEPA 1	1.022780	1.007117	B1/CEPA 1	1.024956	1.008632
B3/V _{Pol} /SDCI+Q	1.021204		B3/CEPA 1	1.028164	1.013193

^aSee text.

Barandiaran et al.^{5b} showed that large basis sets lead to values between 0.8 and 0.85 a.u. whereas minimal basis sets and basis sets with small inner-core parts give values considerably smaller than 0.8 a.u.

Correlation effects amount to about 0.2 a.u. for both species, $\leq 10\%$ of which is contributed by core valence correlation for dimethylzinc. The experiment gives about 1.06 a.u. for this molecule.^{5b} Again the polarization potential on zinc can not faithfully simulate the effect of core valence correlation.

Mulliken Charges

The strong basis set dependency of Mulliken charges can be seen from Table VII. The different nodal structure of the pseudoorbitals for different core definitions also has a significant effect on the Mulliken populations (e.g., see B1, B2 for $M = \text{Zn}$ in Table VII).

Therefore one should only compare Mulliken populations for similar basis sets and a similar valence space.

For the basis set combinations from B2 to B5 this is possible; in each case magnesium has a higher positive charge than zinc, in agreement with chemical experience. A contradictory result of Ratner et al.⁷ can be attributed to an unfortu-

nate choice of geometries in conjunction with too small basis sets (particularly on the metal). Combination B5 shows the same defect when used at the geometries employed in reference 7, while the larger basis sets do not.

Comparison of the Two Dimethyl Compounds

In both molecules the bonding between metal and carbon can be described as semipolar with σ -character. At the SCF-level, neither $p\pi$ -contributions nor contributions from d orbitals (for zinc) play a major role.

For C_{2v} symmetry, the two canonical orbitals that bear the major part of MC-bonding belong to the irreducible representations $b_1(\text{HOMO})$ and a_1 (Fig. 1).

The contribution of the HOMO is responsible for the linear CMC geometry because overlap between the $M - p_x$ -orbital and the ligand orbitals is favored by this arrangement. The removal of an electron from this MO through excitation to the lowest triplet state ($b_1 \rightarrow a_1^*$) consequently leads to a bent geometry. Calculations with B3/CEPA 1 or B3/SDCI+Q show this state to have a CMC-angle of ca. 100° for both molecules, which is consistent with experimental results.²⁴

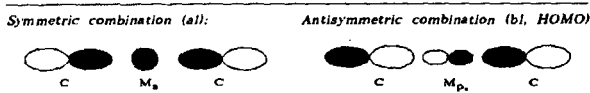
In the magnesium compounds both MOs have a lower population on the metal than for zinc

Table VII. Mulliken atomic gross charges of the dimethyl compounds.

	<i>Dimethylzinc</i>			<i>Dimethylmagnesium</i>		
	Zn	C	H	Mg	C	H
B1	0.308	-0.491	0.112	1.087	-0.871	0.109
B2	0.741	-0.699	0.109	1.023	-0.849	0.112
B3	0.719	-0.508	0.050	0.991	-0.633	0.046
B4	0.737	-0.692	0.108	1.014	-0.813	0.102
B5	0.698	-0.718	0.127	0.848	-0.782	0.119

Table VIII. Mulliken gross populations of the highest occupied MOs in the dimethyl compounds (B4).

$M = \text{Zn}$	Zn	C	H	$M = \text{Mg}$	Mg	C	H
a1	0.640	0.621	0.020		0.472	0.709	0.018
b1	0.336	0.775	0.019		0.303	0.793	0.019

**Figure 1.** Nodal properties of the highest occupied canonical MOs of the dimethyl compounds.

(Table VIII). Consequently the force constant for CMC-bending is considerably smaller in this case (the numerical values in a.u. are: 0.039 (B1), 0.045 (B4) for Mg; 0.077 (B1), 0.063 (B4) for Zn).

Moreover the MC force constants (see Tables III and IV) and the binding energies (see Table X) show the MgC-bond to be weaker.

Together these data strongly support the more ionic character of organomagnesium compounds as compared to organozinc compounds.

Monomethyl Radicals

To study differences arising from the treatment of open shell systems in comparison to the closed shell dimethyl compounds and to get data about the homolytic MC-bond fission, some of the methods used in the preceding section have been applied to the monomethyl radicals of the two metals.

Geometries and Force Constants

No experimental data on geometries and force constants for these open shell systems are available. Our calculated results are listed in Table IX.

The MC bond lengthening effect of valence correlation becomes significantly larger than for the

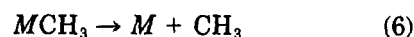
dimethyl compounds. For methylzinc the mutual compensation of valence and core valence correlation effects leads to a relatively good agreement between the SCF values and the B1+/CEPA 1 calculations. If only valence correlation is included (B3/CEPA 1) the ZnC-distance is about 6 pm larger. Correspondingly the force constant for this calculation becomes much smaller than for B1+/CEPA 1, whereas the SCF values are somewhat larger (by 10 to 20%).

Use of the polarization potential improves the ZnC distance as compared to B3/CEPA 1, but the value is still larger than for B1+/CEPA 1.

For methylmagnesium the SCF calculations give too small MgC distances (about 2–3 pm) and force constants about 10 to 20% too large, again. For both radicals, the SCF calculations slightly underestimate the CH-distances and slightly overestimate the MCH-angles (1 pm and 1° respectively).

MC-Bonding Energies

To get a measure of the strength of MC bonds in the dimethyl and monomethyl compounds, the following homolytic bond fission reactions were examined:



For the CH_3 radical the calculated CH distances (109.3 (B1/CEPA 1), 108.5 (B3/CEPA 1), 107.5 (B3) pm, $D3h$ symmetry) were used. The calculated binding energies have not been corrected for zero point vibration.

Table IX. Geometries and MC force constants of the monomethyl radicals.

<i>Methylzinc</i>	R—ZnC [pm]	<ZnCH	R—CH [pm]	k(ZnC) [a.u.]
B1+	201.6	110.5	109.5	0.118
B3	202.1	110.8	109.0	0.104
B1+/CEPA 1	201.0	109.5	110.4	0.096
B3/CEPA 1	207.2	109.5	109.7	0.069
B3/V _{pol} /SDCI+Q	203.4	108.8	109.5	
<i>Methylmagnesium</i>	R—MgC [pm]	<MgCH	R—CH [pm]	k(MgC) [a.u.]
B1	212.7	112.1	109.9	0.089
B3	211.7	112.6	109.5	0.095
B1/CEPA 1	214.5	111.3	110.7	0.077
B3/CEPA 1	214.4	111.4	110.0	0.076

Table X. MC bond dissociation energies [kJ/Mol].

$M = \text{Zn}$	B1+/CEPA 1	B3/CEPA 1	B3/ $V_{\text{Pol}}/\text{SDCI}+\text{Q}$	B3	exp. ^a
$\text{CH}_3\text{Zn}-\text{CH}_3$	-291.7	-248.7	-249.8	-187.8	-289.6
$\text{Zn}-\text{CH}_3$	-47.6	-23.4	-25.5	-1.7	-81.0
$M = \text{Mg}$	B1+/CEPA 1	B1/CEPA 1	B3/CEPA 1	B3	
$\text{CH}_3\text{Mg}-\text{CH}_3$	-248.6	-233.7	-229.1	-162.3	
$\text{Mg}-\text{CH}_3$	-77.7	-64.7	-57.2	-49.2	

^aThe experimental values of Georgiadis et al.²⁶ have error margins of ± 13.4 kJ/Mol.

Table X clearly shows that the energy of homolytic Zn—C bond fission can only be reliably reproduced by calculations that consider a large part of electron correlation including core valence correlation. For the weak ZnC bond in methylzinc even B1+/CEPA 1 gives poor values.

For the magnesium compounds no experimental data are available. As for the other properties of the Mg compounds valence correlation plays a dominant role.

The result of a seemingly higher dissociation energy of the methylmagnesium radical may well be an artifact of the incomplete treatment of correlation for the zinc compounds (even for B1+/CEPA 1). Still these values together with the bond lengths and MC-force constants of the radicals indicate the strengths of the ZnC- and MgC-bond to be much smaller and more similar for these species than for the dimethyl compounds.

CONCLUSIONS

The present calculations allow a comparison of the simplest organometallic compounds of zinc and magnesium. Dimethylmagnesium in its monomeric form has been shown to be more ionic than its zinc analogue. The longer MC bond for $M = \text{Mg}$ is in good agreement with the larger covalent radius tabulated for magnesium.²⁶ But as expected the MgC distance is still much smaller than the one taken from the solid state structure.³ The smaller CMC-bending force constant for $M = \text{Mg}$ as compared to $M = \text{Zn}$ also is consistent with the higher tendency of organomagnesium compounds to polymerize and achieve higher coordination numbers. For the monomethyl radicals the differentiation between the two metals from the present data is less clearcut.

On the SCF level all the pseudopotential/basis set combinations considered give comparable geometries, MC force constants and ionization energies. The atomization energies of the dimethyl compounds show a significant BSSE with the

smallest basis sets considered (B5 which is basically a DZ valence basis set with a small number of primitives for all atoms). Generally the use of this and comparable basis sets is not recommended. The combinations B1 to B3 show similar flexibility, so B3 can be expected to give good results in SCF-calculations on medium-size systems with significant savings in the amount of computer time compared to B1. For large systems B4 seems to be a reasonable compromise.

In addition to the usual bond lengthening effects of valence correlation in main group compounds, for the zinc containing compounds the high polarizability of the 3d shell leads to a valence shell contracting effect of core-valence correlation. For dimethylzinc, therefore, the SCF-values overestimate the ZnC-distance while for methylzinc the even higher core valence- and valence-correlation effects for the ZnC-distance compensate each other to the extent of giving similar ZnC-values in SCF-calculations and calculations considering both correlation components.

A polarization potential in conjunction with the Ar[3d¹⁰]-core pseudopotential on zinc and valence SDCI+Q-calculations can account for parts of the ZnC bond shortening effect of core polarization. The results for dimethylzinc are more encouraging than for the methylzinc radical. Only small parts of the influence of core valence correlation on the energies of ionization, atomization and bonding can be recovered, however, by this means.

This study shows that the *ab initio* calculation of many properties of still larger organozinc and -magnesium compounds with good accuracy seems to be within reach by means of the pseudopotential method.

APPENDIX

All pseudopotential- and basis set parameters used in this article, that have not been published previously, are listed below.

Table XI. Parameters for the zinc 2-valence-electron pseudopotential.¹⁰

<i>l</i>	Exponent	Coefficient	Exponent	Coefficient
0	1.4988024	18.31672	0.7490051	-3.405011
1	1.5327698	11.464304	0.7870907	-1.327391
2	0.7502758	1.583946	0.3747915	0.3333476
3	0.4666989	-0.398428		

Table XII. Basis set parameters.

Element and number of primitives	s-Functions		p-Functions	
	Exponents	Coefficients	Exponents	Coefficients
Zn 4s2p	1.842809	0.122136	0.136715	0.534181
	1.065847	-0.360813	0.042169	0.562075
	0.165116	0.531870		
	0.056048	0.618853		
Zn 3s1p	0.656653	-0.356621	0.085417	—
	0.224679	0.522109		
	0.062077	0.740140		
Mg 4s2p	2.425719	0.026760	0.119701	0.537735
	0.822625	-0.223880	0.038620	0.552139
	0.107749	0.620464		
	0.039485	0.498607		
Mg 3s1p	1.616690	0.141138	0.076427	—
	1.110157	-0.302593		
	0.070333	1.050649		
C 4s4p	2.581190	-0.289364	8.257547	0.042311
	1.596882	0.209015	1.960285	0.211185
	0.408595	0.601018	0.551454	0.500500
	0.138945	0.451515	0.155007	0.469981
C 3s3p	3.083822	-0.170171	4.363067	0.108191
	0.558944	0.537878	0.906016	0.456769
	0.186420	0.588679	0.219441	0.627747

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