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Preliminary communication

USE OF ^{91}Zr-NMR FOR CHARACTERIZATION OF THE ELECTRONIC ENVIRONMENT IN ORGANOZIRCONIUM COMPOUNDS

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Summary

The ^{91}Zr chemical shifts of organozirconium compounds with π-ligands such as η^8-cyclooctatetraene, η^5-cyclopentadienyl, η^3-allyl, and η^4-butadiene involve distinctly different ranges for 16- and 18-electron environments at Zr. Alkyl substitution of the π-ligands leads to changes in δ(^{91}Zr) corresponding to the alterations in mean excitation energies of the complexes, indicating that in high valent zirconium compounds the ^{91}Zr shifts are governed by paramagnetic shielding.

Since the advent of multinuclear NMR spectroscopy a correlation between the formal oxidation state and the chemical shift has been found for many metals [1]. Transition metal π-complexes may exist in and rearrange to a variety of oxidation states and therefore transition-metal NMR can be expected to provide a sensitive probe for their characterization. There have been some systematic NMR studies for organometallic compounds of the late transition metals [2], but NMR investigations of the Subgroup IV metals are rare, probably in part owing to their unfavourable NMR properties. To our knowledge there are as yet no HF-NMR data available. For ^{47,49}Ti [3] and ^{91}Zr [4] very few reports on halogen containing systems have appeared. On the other hand, π-complexes of Zr are of considerable chemical interest, e.g. (η^8-cyclooctatetraene)zirconium complexes [5] catalyse the stereospecific dimerization of butadiene and 3,3-dimethylcyclopropene. Very recently, (mono-η^5-cyclopentadienyl)zirconium complexes with various π-ligands have become available [6]. They may be obtained as chiral species and are of particular interest as Ziegler-type catalysts for C—C bond formation in polymerisation reactions. Thus for both spectroscopic and chemical reasons we have become interested in determining the chemical shift range and line widths of

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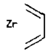
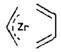
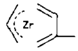
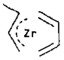
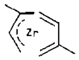
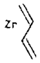
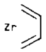
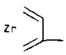
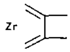
the ^{91}Zr resonance in such π-complexes. It was hoped that besides providing characteristization of the electronic environment of those complexes it might be possible to find some simple trends in the ^{91}Zr chemical shifts.

The ^{91}Zr chemical shifts and linewidths for 12 organometallic zirconium compounds are listed in Table 1.

TABLE 1

^{91}Zr NMR CHEMICAL SHIFTS AND LINE WIDTHS $W_{1/2}$ FOR THE ORGANOZIRCONIUM COMPOUNDS I—XII AT 37.21 MHz (which corresponds to 400.13 MHz for ^1H) (T 310 K, external standard I, dissolved cf. a, $\delta(^{91}Zr)$ I $\equiv$ 0. Typical recording times of 0.5 molar samples are several minutes. Cp = η^5-cyclopentadienyl, Me_5Cp = pentamethyl-η^5-cyclopentadienyl. COT = η^8-cyclooctatetraene)

Compound		Solvent	$\delta(^{91}Zr)$ (ppm)	$W_{1/2}$ (Hz)
Cp_2ZrBr_2	I	^{a}	0	15
Cp_2ZrCl_2	II	^{a}	—113	250
$Cp_2ZrCl(vinyl)$	III	^{a}	+16	1250
$(Me_5Cp)_2ZrCl_2$	IV	^{a}	+82	90
COT 	V	^{b}	+148	220
Cp 	VI	^{b}	+90	1400
Cp 	VII	^{b}	+132	1400
Cp 	VIII	^{b}	+142	2500
Cp 	IX	^{a}	+268	1000
Cp_2 	Xa	^{c}	—384	3100
Cp_2 	Xb	^{c}		
Cp_2 	XI	^{c}	—324	2200
Cp_2 	XII	^{c}	—257	1900

^{a} Solvent THF + 10% C_6D_6. ^{b} Solvent toluene-d_8. ^{c} Solvent benzene-d_6.

The NMR-parameters for I and II agree well with literature values [4a]. Substitution of one chlorine atom by a vinyl group leads to lower shielding of ^{91}Zr in Cp_2ZrXR ($R = C_2H_3$). This immediately indicates that a simple interpretation in terms of eletropositive versus electronegative substituent effects on $\delta(^{91}Zr)$ is unsatisfactory. Replacement of the Cp-hydrogens by methyl groups leads to significantly larger δ-values for IV, compared to II, a further indication that the ^{91}Zr chemical shifts in these compounds cannot be interpreted in terms of simple changes in the electron density. The deshielding in IV, however, can be rationalized if attention is focused on the dependence of $\delta(^{91}Zr)$ on the average excitation energy ΔE. According to Ramsey's shielding theory [7] the NMR shielding σ (the screening constant σ is proportional to $-\delta$) is given by eq. 1, where A is the diamagnetic and $B/\Delta E$ is the paramagnetic

$$\sigma = A - B/\Delta E \qquad (1)$$

term of the chemical shift (B is the angularmomentum factor). When the cyclopentadienyl bears methyl groups, the binding energies of the $3d_{3/2}$ and $3d_{5/2}$ inner shell electrons and of the valence electrons decrease [8]. In view of the place of Zr in the Periodic Table and of its 16 electron configuration in compounds I—IV, the permethylation of Cp should lower the mean excitation energy ΔE and the shielding for IV when compared to II [9].

The 16-electron complexes V—IX contain only π-ligands. The solution structure of V [5,10] and the thermodynamic isomers of the monocyclopentadienylzirconium compounds V—IX have been investigated recently by ^{1}H and ^{13}C NMR spectroscopy [6,11], and in the case of VI also by X-ray analysis [6]. Apparently, substitution of a hydrogen by a methyl group in the π-ligand causes a ^{91}Zr low-field shift of 40 to 60 ppm. The substituent effects seem to be additive, as suggested by comparing $\delta(^{91}\text{Zr})$ of II with IV and within the series VI—IX. Again, the general trend of the ^{91}Zr chemical shifts in VI—IX can qualitatively be explained in terms of the ΔE-dependence of σ as expressed by eq. 1, e.g. ΔE decreases going from butadiene to isoprene [12].

The butadienedicyclopentadienylzirconium complexes exist as different isomers Xa and Xb [10,13]. In ^{91}Zr NMR a 1/1 mixture of X gives a broad resonance at —384 ppm, and even at higher temperatures individual shifts of Xa and Xb could not be resolved. In complexes XI and XII the diene has η^4-*s-cis* configuration; methyl-substitution in this ligand causes a ^{91}Zr low field shift of the same order of magnitude as in the series VI—IX. The most striking feature of $\delta(^{91}\text{Zr})$ for X—XII, however, is the extremely strong shielding of the metal. Because the ^{91}Zr shifts do not alter much when the η^8-cyclooctatetraene ligand is replaced by a combination of a η^5-cyclopentadienyl and an η^3-allyl ligand we attribute the low δ-values for X—XII as due to the 18-electron configuration of these complexes. This environment leads to a better screening of the metal and disfavours low lying excited electronic states.

Since the ^{91}Zr shifts of the organometallic compounds V—XII cover a range of more than 600 ppm, and typical line widths are of several hundred Hz, high field ^{91}Zr NMR may become a valuable tool for structural investigations. Moreover, the differing ^{91}Zr shifts for 16- and 18-electron configuration in V—IX and X—XII, respectively, lead to optimism about the possibility of being able to follow catalytic reactions by ^{91}Zr NMR.

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