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Zirconium-91 Nuclear Magnetic Resonance Spectroscopy: the First Chemical Study

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Zirconium-91 NMR signals have been observed for the series Cp_2ZrX_2 (X = Cl, Br, I) and ZrX_6^{2-} (X = F, Cl) ions, and an inverse halogen dependence has been found. The Carbon-13 NMR of the fluxional molecule Cp_4Zr is also reported.

Introduction

The burgeoning interest in the organometallic chemistry of zirconium [1] and its current utility in organic synthesis [2] prompted us to investigate the environment of the central metal atom. To our surprise, the ^{91}Zr nucleus (11.23% abundant; I = 5/2) [3] seems not to have been exploited by NMR spectroscopists [4]. The recent determination [5] of the quadrupole moment of ^{91}Zr ($Q = -0.21 \times 10^{-28}$ m^2) would suggest that a symmetrical environment may be necessary to obtain spectra with acceptable line widths. The ^{19}F spectrum of the ZrF_6^{2-} ion has a reported peak width at half height of 8 Hz and, unlike the SnF_6^{2-} and other analogous systems, shows no metal-fluorine coupling [6]. This is perhaps not surprising since the proclivity of Zr to adopt seven- and eight-fold coordination [7] makes the obtention of a discrete octahedral ZrF_6^{2-} ion in aqueous solution an unlikely circumstance. We now present the first ^{91}Zr nmr study and indicate its potential utility in inorganic and organometallic chemistry.

Discussion

To our knowledge, the only report [3] of ^{91}Zr nuclear magnetic resonance data involved a measurement of the relaxation time of an aqueous D_2O solution of $(NH_4)_2ZrF_6$ which was found to be approximately 10^{-3} s and, if $T_1 = T_2$, this corresponds to a linewidth of *ca.* 318 Hz. We have repeated this experiment and find that, in appropriate circumstances, ^{91}Zr resonances are readily obtained in acceptable time periods (see Fig. 1).

We found that the ^{91}Zr resonance in ZrF_6^{2-} was extremely sensitive to changes in the Zr:F ratio and in this respect it parallels the behaviour of the ^{19}F resonances which can be broadened to 1500 Hz as excess fluoride is added [6]. The minimum half-width we have observed for the ^{91}Zr resonance was 50 Hz and this corresponded to a 13 Hz half-width for the ^{19}F spectrum. In neither case was Zr–F coupling observed supporting the idea of a system undergoing rapid fluoride exchange, probably via a seven-coordinate intermediate.

TABLE I. ^{91}Zr and ^{13}C Chemical Shifts and Linewidths.

	^{91}Zr (ppm)[a]	^{91}Zr Half-widths (Hz)	^{13}C (ppm)[b]
Cp_2ZrCl_2	−121.9	276 ± 10	116.2
$Cp_2ZrClBr$	−65.9	237 ± 10	–
Cp_2ZrBr_2	0.0	19 ± 2	116.2[c]
Cp_2ZrI_2	126.0	134 ± 10	115.1
Cp_4Zr	–	–	113.5 (½ width 2 Hz) 113.1 (½ width 36 Hz)
$(NH_4)_2ZrF_6$[d]	−191.1	50 ± 5	–
H_2ZrCl_6e	601.2	245 ± 10	–

[a] Relative to Cp_2ZrBr_2 in THF. [b] Relative to TMS; solvent $CDCl_3$. [c] In THF. [d] In D_2O as solvent. [e] In conc. HCl.

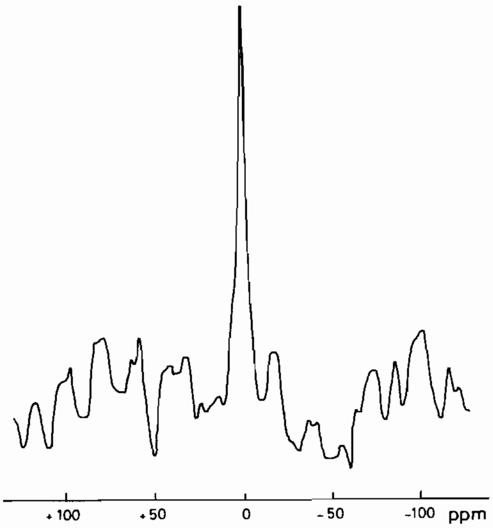

Fig. 1. 8.37 MHz ^{91}Zr nmr spectrum of Cp_2ZrBr_2 in THF; 1840 transients (total accumulation time 5 min).

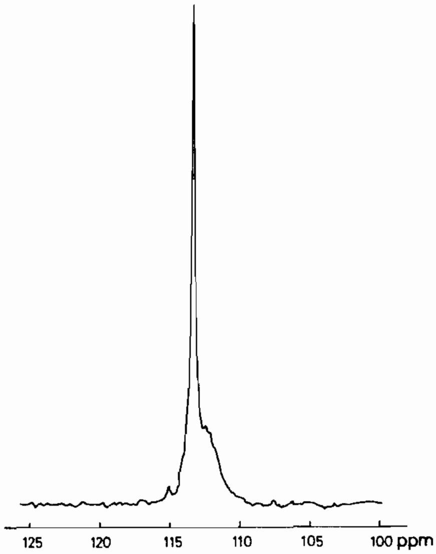

Fig. 2. 20.115 MHz ^{13}C nmr spectrum of Cp_4Zr in $CDCl_3$ at 35 °C.

The 'normal' halogen dependence on the chemical shifts of the tri- and tetra-halides of the main group III and IV elements is such that the more electronegative halides deshield the central metal and so fluoride complexes resonate at higher frequencies (lower fields) than the analogous iodides [8]. Recently, an 'inverse' halogen dependence has been observed for the d^0 halide derivatives of ^{47}Ti(IV) [9], ^{93}Nb(V) [10] and ^{183}W(VI) [11] and it has been suggested [10] that this phenomenon results from d-orbital participation in the metal–halogen bond where transition metals are involved. As is shown in Table I, the inverse halogen effect occurs also for all the ^{91}Zr(IV) complexes studied.

Although ^{55}Mn and ^{59}Co chemical shifts show normal halogen dependence [8], the data refer only to low valent systems in which the metal is also coordinated to π-acid ligands which might well preclude any metal d-orbital participation in the metal–halogen bond. Interestingly, when ^{183}W is in a low oxidation state in the $(C_5H_5)W(CO)_3X$ system, the halogen dependence is normal [12]. These data suggest that only in high oxidation states (preferably with d^0 electronic configurations) will the more electronegative halides give lower frequency absorptions.

Of interest to organometallic chemists is in the series Cp_2ZrX_2 for which data are presented in Table I. The narrowest line so far obtained is that for Cp_2ZrBr_2 (Fig. 1), which has a T_1 value of $\sim 17 \times 10^{-3}$ sec, and which we have chosen as our temporary standard. Undoubtedly, a more convenient reference molecule will emerge in the near future. Since the Cp_2ZrX_2 systems are at best C_{2v}, it seems not unreasonable to expect a narrow line for the fluxional molecule Cp_4Zr which shows a single proton resonance even at 123 K [13]. However, the ^{91}Zr resonance for this molecule is so broad as to escape detection thus far.

The Cp_4Zr molecule has provoked much discussion [14, 15] and recent structural results [16] show that, while one ring is genuinely monohapto, the other three are symmetrically h^5-bonded but at such a distance that they may be considered to donate sufficient electrons to raise the electron count around the zirconium only to 18 rather than 20. Our ^{13}C nmr data go some way to supporting this view since over the temperature range 163–348 K the spectrum (see Fig. 2) scarcely changes and shows a sharp (½ width 2 Hz) singlet (5 C) positioned on a broad (½ width 36 Hz) peak (15 C); the proton-coupled spectrum shows that the average $^1J_{CH}$ values for both types of ring are ~167 Hz. We interpret these spectra to mean that, while the exchange between the σ-bonded h^1-Cp ring and the three π-bonded rings is slow on the ^{13}C nmr time scale [17, 18], the metallotropic shift of Zr around the h^1-ring is still too rapid to be stopped. These data are entirely consistent with the ^{91}Zr nmr and infrared spectroscopic [14] results which indicate the Zr environment to be non-tetrahedral.

The ^{91}Zr spectra of a broader range of molecules will be reported elsewhere.

Experimental

All the molecules were synthesized by literature methods [1]. ^{91}Zr nmr spectra were obtained on a Bruker WH90 spectrometer operating at 8.37 MHz at 25 °C.

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17 For Cp_4Ti, the activation energy for the σ–π exchange of the rings is ~16 kcal/mol; clearly, it must be considerably less for the Cp_4Zr system.

18 It is an interesting thought that the transition state for the σ–π exchange of the Cp rings in Cp_4Ti may be the ground state for Cp_4Zr, and *vice versa.*