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Preliminary communication

THE PMR SPECTRUM OF BIS(π-TETRAHYDROINDENYL)ZIRCONIUM DIHYDRIDE DIMER: A NEW COMPOUND WITH AN UNUSUALLY LOW FIELD HYDRIDO RESONANCE

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Summary

The title compound has two magnetically distinct pairs of hydrido groups; one gives rise to a ^{1}H NMR signal at δ —1.56 (i.e. upfield from TMS), whereas the other is downfield at δ 4.59.

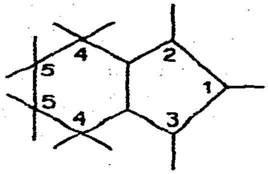
Alkylcyclopentadienylzirconium compounds catalyse hydrogenation of alkenes (20—100 atm H_2/50—120°) [1], but in the absence of the alkene, hydrogen converts the alkylzirconiums into insoluble, white hydrides. Hydrogenation of dimethyldi-π-indenylzirconium by hydrogen gas (80 atm/140°/8 h) in benzene proceeds similarly and gives the title compound, presumably via di-π-indenylzirconium dihydride which plays an autocatalytic role in this reaction. The yield is essentially quantitative. It is readily soluble in aromatic hydrocarbons and ethers (but not in petroleum ethers) and is dimeric in freezing benzene. Satisfactory C, H, total ash and hydridic hydrogen analyses were obtained.

The compound had Zr—H infrared bands at 1545 and 1285 cm^{-1} in both C_6D_6 solution or KBr discs. In the dimeric bis(π-tetradeuteroindenyl)zirconium dideuteride, the corresponding Zr—D bands were at 1104 and 932 cm^{-1} respectively. These frequencies are comparable with those found for di-π-cyclopentadienylzirconium dihydride [ν(Zr—H) 1520 and 1300 cm^{-1}; ν(Zr—D) 1100 and 960 cm^{-1}] which was considered to be polymeric with bridging hydrido groups [2].

Table 1 gives details of the PMR spectrum of the title compound. The most important feature of the PMR data is the abnormally low field value for the Zr—H_A protons. While the band at δ —1.56 can be assigned a priori to a hydrido species [3], the low field position (δ 4.59) of the H_A protons would tend to preclude a like assignment being made for this resonance. However, both peaks

TABLE 1

PMR SPECTRAL DATA [a] FOR BIS(π-TETRAHYDROINDENYL)ZIRCONIUM DIHYDRIDE DIMER IN $C_6D_5CD_3$ AT 30°

		δ (rel. TMS)	Rel. Intensity
Tetrahydroindenyl protons			
	H(1)	5.97 (tr)	4
	H(2)	5.60 [b]	4
	H(3)	5.01 [b]	4
	H(4)	2.60 [c]	16
	H(5)	1.77 [c]	16
Zirconium-hydrido protons			
	H_A	4.59 [d]	2
	H_B	−1.56 [e]	2

[a] Measured on Varian HA-100 spectrometer. [b] Moderately broad bands; coalesce at 110°. [c] Broad multiplets. [d] Triplet (J 7Hz) below −10°. [e] Triplet (J 7Hz) below −36°, centered at δ −1.68.

are essentially absent* in the PMR spectrum of bis(π-tetradeuteroindenyl) zirconium dideuteride, but are regenerated by reaction with hydrogen (80 atm/ 30°/24 h). The δ 4.59 and δ −1.56 signals of the dihydrido compound diminish on deuteration under similar conditions.

At 30° H_A and H_B protons are exchanging as irradiation at one hydrido resonance frequency induces the complete disappearance of the other hydrido signal. This exchange is not evident at −36°, and the two peaks, now triplets, can be decoupled from each other. The two H_A protons are therefore magnetically equivalent as are the two H_B protons. As both pairs are attached to the zirconium atoms in the dimer at least one pair exists as μ-hydrido groups**. While the hydrido exchange processes between the protons H_A and H_B and within H_A are sufficiently retarded at −10° to enable the H_A signal to be observed as a triplet (J 7Hz), the exchange process within H_B continues until −36°.

The non-equivalence of the indenyl H(2) and H(3) protons has been observed previously [4] in the μ-oxo compound $[\pi\text{-(tetrahydroindenyl)}_2ZrCl]_2O$. The H(2) and H(3) protons are coupled to H(1). Whereas the H(1) band is little affected on heating (triplet at 120°, J 3.5 Hz, the H(2) and H(3) bands broaden, coalescing at 110° into a band at δ 5.33 which can be resolved into a doublet (J 3.5 Hz) at 120°. The H_B hydrido band disappears into the base line at 50°, but the H_A band can be observed up to about 90°.

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References

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*The D_2 gas contained some H_2 and HD impurity.

**In the dimer $[CpZrH_2 \cdot AlMe_3]_2$, which has both a pair of bridging Zr—H—Zr and Zr—H—Al groups, the hydrido PMR resonances are in the range δ −0.9 to δ −3.0 [3]. Whether both the H_A and H_B hydrogens are bridging, as the infrared data would suggest, awaits a molecular structure determination which is now being undertaken in these laboratories.