

## Crystal and Molecular Structure of Tetra(cyclopentadienyl)zirconium

Sir:

The chemistry of cyclopentadienyl derivatives of the early transition metals has come under close scrutiny over the past several years. One of the most perplexing problems has concerned the structures of  $(C_5H_5)_4Zr$  and  $(C_5H_5)_4Hf$ .  $^1H$  NMR investigation<sup>1</sup> revealed only a single sharp resonance down to  $-150$  °C, but IR spectral studies indicated that the local symmetry of the metal atom was less than tetrahedral.<sup>1</sup> In an effort to clarify the nature of the zirconium-ring bonding, Kulishov et al. described the x-ray crystallographically determined structure of  $(C_5H_5)_4Zr$  in 1970.<sup>2</sup> There were reputedly three rings bound in an  $\eta^5$  fashion, and one held by an  $\eta^1$  linkage. Unfortunately, the quality of the work was so low that no credence could be given to the result.<sup>3</sup> In addition to the obvious crystallographic difficulties, questions concerning two other points were raised. (1) Zirconium and hafnium organometallic compounds are invariably isostructural,<sup>4</sup> but  $(C_5H_5)_4Zr$  (space group  $P2_12_12_1$ )<sup>2</sup> was unlike either  $(C_5H_5)_4Hf$  (two  $\eta^5$ - $C_5H_5$ , two  $\eta^1$ - $C_5H_5$  rings in space group  $P4_21m$ )<sup>5</sup> or  $(C_5H_5)_4Ti$  (two  $\eta^5$ - $C_5H_5$ , two  $\eta^1$ - $C_5H_5$  rings in  $P6_122$ ).<sup>6</sup> (2) The effective atomic number of zirconium would be 20 for the reported structure. To avoid this electronic anomaly Calderon, Cotton, DeBoer, and Takats<sup>6</sup> proposed that  $(C_5H_5)_4Zr$  contains one  $\eta^1$ - $C_5H_5$  ring, one  $\eta^5$ - $C_5H_5$  ring, and two rings tilted in such a manner as to contribute 4 electrons each. To resolve this controversy we have carried out an accurate x-ray crystallographic study of  $(C_5H_5)_4Zr$ , and the results are given herein. The structure consists of one  $\eta^1$ - $C_5H_5$  ring, and three  $\eta^5$ - $C_5H_5$  rings which are bonded to the zirconium atom at a much longer distance than that normally found for a  $Zr-(\eta^5-C_5H_5)$  interaction. The molecule is shown in Figure 1.

Tetra(cyclopentadienyl)zirconium was prepared by the reaction of  $(\eta^5-C_5H_5)_2ZrCl_2$  with  $NaC_5H_5$  in diethyl ether. Crystals suitable for the x-ray diffraction study were grown by the slow cooling of a toluene solution. A yellow-orange crystal of the compound was sealed in a thin-walled glass capillary. The space group is  $C2/c$ ,<sup>7</sup> and the lattice parameters are  $a = 13.332$  (5),  $b = 9.065$  (4),  $c = 25.684$  (6) Å;  $\beta = 103.40$  (3)°; and  $\rho_{calcd} = 1.53$  g cm<sup>-3</sup> for  $Z = 8$ . Data collection<sup>8</sup> yielded 1461 observed reflections, and the least-squares refinement produced a final agreement index of  $R = \Sigma(|F_o| - |F_c|)/\Sigma|F_o| = 0.046$ . Hydrogen atoms were included, and all nonhydrogen atoms were refined with anisotropic thermal parameters.

In the three  $\eta^5$ - $C_5H_5$  groups the  $Zr-C$  bond distances show significant variations from the mean of 2.58 (3) Å. For R1 the average is 2.56 (3) Å and the range is 2.517 (10) to 2.583 (7) Å; for R2, 2.59 (2) and 2.562 (6) to 2.619 (7) Å; for R3, 2.60, and 2.556 (7) to 2.634 (8) Å. R2 and R3 are planar to within 0.008 Å, but R1 (because of the carbon atom involved in the  $Zr-C$  length of 2.517 (10) Å) is only planar to 0.04 Å. The spread of  $Zr-C$  bond distances is large, but a similar range is often seen in complexes with bulky cyclopentadienyl-like ligands. In  $(\eta^5-C_9H_7)_2Zr(CH_3)_2$ ,<sup>9</sup> the  $Zr-C(\eta^5)$  lengths range from 2.502 (6) to 2.622 (5) Å. However, in compounds of the general type  $(\eta^5-C_5H_5)_2ZrR_2$ , the range is more narrow, and the mean  $Zr-C(\eta^5)$  length is shorter even for very large  $\sigma$  bonded R groups: 2.513 (15) Å in  $(\eta^5-C_5H_5)_2Zr-[CH(C_6H_5)_2]_2$ ,<sup>10</sup> 2.515 (19) Å in  $(\eta^5-C_5H_5)_2Zr-[CH_2C(CH_3)_3]_2$ ,<sup>11</sup> 2.524 (22) Å in  $(\eta^5-C_5H_5)_2Zr-[CH_2Si(CH_3)_3]_2$ ,<sup>11</sup> 2.543 (14) Å in  $(\eta^5-C_5H_5)_2Zr-[CH(Si(CH_3)_3)]_2(C_6H_5)$ .<sup>11</sup>

The  $\eta^1$ - $C_5H_5$  ligand is bonded in a  $\sigma$  fashion to the zirconium atom. The  $Zr-C$  bond vector makes an angle of 49° with the

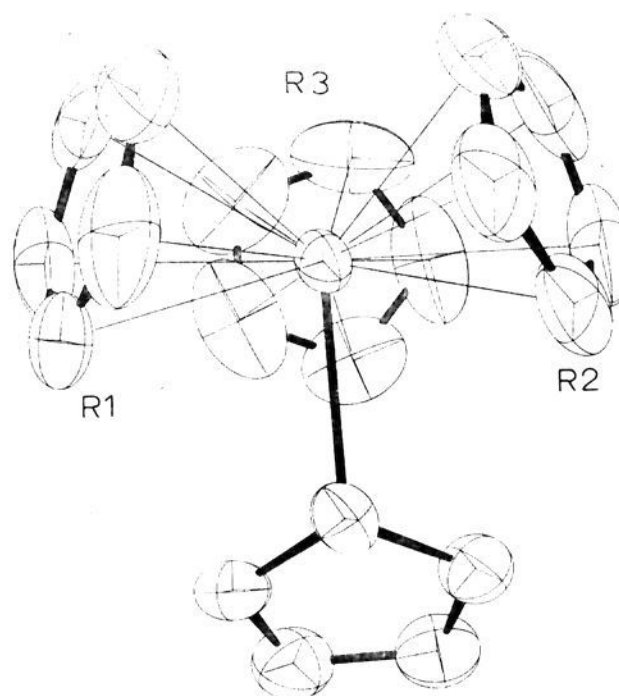


Figure 1. Molecular structure of  $(\eta^5-C_5H_5)_3(\eta^1-C_5H_5)Zr$  with the atoms represented as their 50% probability ellipsoids for thermal motion.

plane of the cyclopentadienyl ring. The  $Zr-C(\eta^1)$  length, 2.447 (6) Å, is  $\sim 0.2$  Å longer than the  $Zr-C(\text{alkyl})$  distances in compounds such as  $(\eta^5-C_9H_7)_2Zr(CH_3)_2$  (2.255 (5) Å)<sup>9</sup> and  $(\eta^5-C_5H_5)_2Zr[CH_2Si(CH_3)_3]_2$  (2.280 (4) Å),<sup>11</sup> but is similar to the 2.388 (12) Å average in  $(\eta^5-C_5H_5)_2Zr[CH(C_6H_5)_2]_2$ .<sup>10</sup> It is possible therefore to describe the  $Zr-C(\eta^1)$  bond as a  $\sigma$  bond in a very crowded environment. The parameters of the cyclopentadienyl ligand itself conform closely to the expected diene structure.<sup>6</sup>

Tetra(cyclopentadienyl)zirconium(IV) falls between the two extremes exemplified by  $(\eta^5-C_5H_5)_2Ti(\eta^1-C_5H_5)_2$ <sup>6</sup> and  $(\eta^5-C_5H_5)_4U$ .<sup>12</sup> The 4+ ionic radii are given<sup>13</sup> as 0.68 Å for  $Ti^{4+}$ , 0.74 Å for  $Zr^{4+}$ , and 0.93 Å for  $U^{4+}$ . Even though the  $U^{4+}$  ionic radius is 0.19 Å larger than that of  $Zr^{4+}$ , it is still not possible to place four  $\eta^5$ - $C_5H_5$  groups around the uranium atom at a normal bond distance. The  $U-C(\eta^5)$  lengths average 2.81 Å, whereas the equivalent separation is typically 2.73 Å in compounds of the type  $(\eta^5-C_5H_5)_3UR$ .<sup>14</sup>

The angles which involve the centroids of the cyclopentadienyl rings are similar to those found for  $(\eta^5-C_5H_5)_3UR$ . For  $(\eta^5-C_5H_5)_3UC\equiv CC_6H_5$ <sup>15</sup> the centroid-U-centroid angles average 117°, and those of the centroid-U- $C(\eta^1)$ , 100°. For  $(C_5H_5)_4Zr$  the values are 115, 116, and 119° for the centroid-Zr-centroid angles and 99, 99, and 101° for the centroid-Zr- $C(\eta^1)$  angles.

The final configuration of cyclopentadienyl complexes of the early transition metals represents a balance between the need to fill the coordination sphere and intramolecular steric effects. The effective atomic number of the zirconium atom in  $(C_5H_5)_4Zr$  can be rationalized in a manner similar to that used by Cotton for  $(C_5H_5)_3Mo(NO)$ .<sup>16</sup> If the  $C_5H_5^-$  ring is assumed to contribute 5 electrons to a zirconium atom when bonded at a  $Zr-C(\eta^5)$  length of 2.51 Å, then it is reasonable to view the contribution as somewhat less at a  $Zr-C(\eta^5)$  separation of 2.58 Å. In the present case a count of 18 electrons would be obtained if each  $\eta^5$ -cyclopentadienyl carbon atom adds  $\sim 0.9$  electron to the metal.

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### References and Notes

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- (3) The situation with regard to the study described in ref 2 is described in an appendix to ref 6.
- (4) In the four complete x-ray crystallographic studies available,  $(\text{CH}_2)_3(\eta^5\text{-C}_5\text{H}_4)_2\text{MCl}_2$  (C. H. Saldarraga-Molina, A. Clearfield, and I. Bernal, *J. Organomet. Chem.*, **80**, 79 (1974)),  $(\eta^5\text{-C}_9\text{H}_7)_2\text{M}(\text{CH}_3)_2$  (ref 9),  $(\eta^5\text{-C}_5\text{H}_5)_2\text{MC}_4(\text{C}_6\text{H}_5)_4$  (M = Zr, J. L. Atwood, W. E. Hunter, and C. Fiorani, unpublished results; M = Hf, J. L. Atwood, W. E. Hunter, H. Alt, and M. D. Rausch, *J. Am. Chem. Soc.*, **98**, 2454 (1976)), and  $(\eta^5\text{-C}_5\text{H}_5)_2\text{M}[\text{CH}(\text{C}_6\text{H}_5)_2]_2$  (ref 10), the compounds for M = Zr and Hf are isostructural.
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- (7) The molecular structure of  $(\text{C}_5\text{H}_5)_4\text{Zr}$  described in this work is essentially the same as that found by the Russian investigators.<sup>2</sup> However, the assignment of the monoclinic space group  $C2/c$  in the present study means that the previous work was based on a different crystalline modification, a twinned crystal, or a different compound.
- (8) Details of the data collection procedure have been previously described.<sup>9</sup> The structure was solved by the straightforward application of standard heavy-atom techniques.
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### $\mu$ -Carbonyl- $\mu$ -hydrido-decacarbonyltriferic Acid, $\text{H}_2\text{Fe}_3(\text{CO})_{11}$

Sir:

We report the preparation, properties, and NMR studies of  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ , the first example of a metal carbonyl hydride in which a proton is bonded to the oxygen of a carbon monoxide ligand.

A compound formulated as  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  was first reported by Hieber and Brendel in 1957 but was not completely characterized.<sup>1</sup> Later Green made reference to unpublished results by Davison and Wilkinson who found a single high-field hydride resonance 14.9 ppm relative to  $\text{Me}_4\text{Si}$  for both  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  and  $\text{HFe}_3(\text{CO})_{11}^-$ .<sup>2</sup> Attempts in our laboratory to prepare  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  by Hieber and Brendel's method, which involves treating an ether solution of  $\text{Fe}_3(\text{CO})_{11}^{2-}$  with aqueous acid, yielded a solution having a high-field proton resonance at 15.0 ppm relative to  $\text{Me}_4\text{Si}$ , which confirms Davison and Wilkinson's observations. Infrared absorptions were observed at 2062 (w), 2048 (vw), 2000 (vs), 1990 (s), 1953 (ms), 1942 (ms), 1750 (m). These frequencies correspond to the  $\text{HFe}_3(\text{CO})_{11}^-$  ion.

This ether solution also contains IR bands at  $\sim 3500$  and  $1640\text{ cm}^{-1}$  and a weak broad  $^1\text{H}$  NMR signal around  $\delta_{\text{H}}$  6.7 ppm ( $\text{Me}_4\text{Si}$ ), which are in the range of  $\text{H}_3\text{O}^+$  or higher aggregates.<sup>3,4</sup> Based on these data, the best formulation for the material first reported by Hieber and Brendel is  $[\text{H}_3\text{O} \cdot n\text{H}_2\text{O}][\text{HFe}_3(\text{CO})_{11}]$ . Attempts to remove water by passing ether-saturated oxygen-free  $\text{N}_2$  through the red solution lead

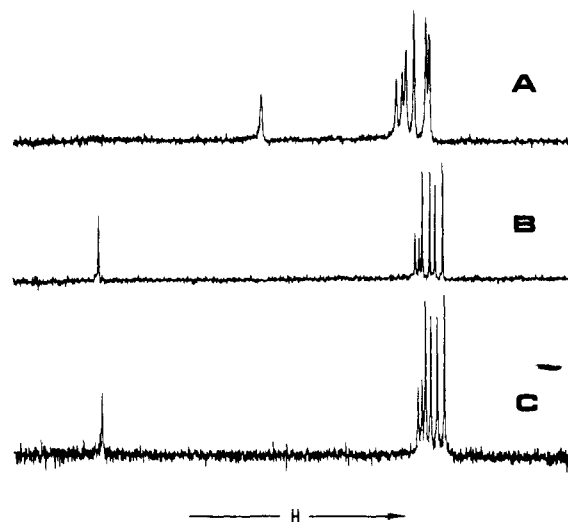
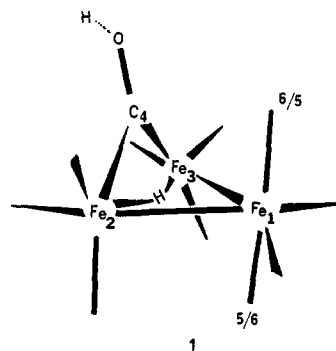


Figure 1. Low-temperature  $^{13}\text{C}$  NMR spectra of (A)  $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$  ( $-120^\circ\text{C}$ ), (B)  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  ( $-100^\circ\text{C}$ ), and (C)  $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$  ( $-100^\circ\text{C}$ ).

to reduction of the water content, but, before the water was completely removed, decomposition occurred, as judged by a sudden change in color and IR spectrum.

To prepare anhydrous  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ , a solution containing 0.036 mmol of  $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$  in 0.6 mL of dry and air-free  $\text{CD}_2\text{Cl}_2$  was prepared and cooled to  $-90^\circ\text{C}$  ( $\text{PPN}$ , bis(triphenylphosphine)iminium cation). To this cooled solution 0.036 mmol of fluorosulfuric acid was added under nitrogen. The reaction proceeded rapidly to give a dark red-violet solution, which decomposed around  $-30^\circ\text{C}$  to a compound identified as  $\text{Fe}_3(\text{CO})_{12}$  by color and infrared spectrum. NMR evidence, which is described below, demonstrated that the red-violet compound is  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  having an unusual structure, **1**.



$^1\text{H}$  NMR spectra of  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  in  $\text{CD}_2\text{Cl}_2$  were recorded in the range of  $-80$  to  $-30^\circ\text{C}$ . Unlike the results obtained for  $[\text{H}_3\text{O}^+ \cdot n\text{H}_2\text{O}][\text{HFe}_3(\text{CO})_{11}^-]$ , the hydridic proton is observed at  $\delta -18.4$  ppm. At  $-80^\circ\text{C}$  an additional proton signal is observed at  $\delta 15.0$  ppm, which shifts upfield to  $\delta 13.8$  ppm at  $-40^\circ\text{C}$ . These data are consistent with metal-bound ( $-18.4$  ppm) and oxygen-bound ( $15.0$  ppm) protons in  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ . For reference, the  $^1\text{H}$  NMR spectrum of  $\text{HSO}_3\text{F}$  in  $\text{CD}_2\text{Cl}_2/\text{Me}_4\text{Si}$  is found at  $\delta 10.5$  ppm at  $-80^\circ\text{C}$  and  $10.1$  ppm at  $-40^\circ\text{C}$ .

Further evidence for the nature of  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  was obtained by a comparison of the  $^{13}\text{C}$  NMR spectra of  $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ ,<sup>5</sup>  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ , and  $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$  (Figure 1, A, B, and C, respectively). A sample of  $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$  enriched to  $\sim 10\%$   $^{13}\text{C}$  per molecule was used to generate anhydrous  $\text{H}_2\text{Fe}_3(\text{CO})_{11}$  in a  $\text{CH}_2\text{Cl}_2/\text{CD}_2\text{Cl}_2$  (3:1) mixture, and  $^{13}\text{C}$  NMR spectra were recorded in the