

Struct. Chem. (Eng. Transl.), **11**, 646 (1970).

- (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(M = Zr, J. L. Atwood, W. E. Hunter, and C. Fioriani, unpublished results; M = Hf, J. L. Atwood, W. E. Hunter, H. Alt, and M. D. Rausch, *J. Am.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.
- (5) V. I. Kulishov, N. G. Bokly, and Yu. T. Struchkov, *J. Struct. Chem. (Engl. Transl.)*, **13**, 1029 (1972); V. I. Kulishov, E. M. Brainina, N. G. Bokly, and Yu. T. Struchkov, *J. Organomet. Chem.*, **36**, 333 (1972). The actual situation with respect to the space group of $(\text{C}_5\text{H}_5)_4\text{Hf}$ is presently in a state of some confusion. In ref 2 it was given as $P4_21m$ (sic), $P4_212$, or $P4_22_12$. In the reference quoted herein it was assigned to $P4_21m$. It is clearly not the same as the C_2/c found for $(\text{C}_5\text{H}_5)_4\text{Zr}$. In view of the crystallographic disorder and overall poor quality of the derived structure of $(\text{C}_5\text{H}_5)_4\text{Hf}$, a new determination is in order.
- (6) J. L. Calderon, F. A. Cotton, B. G. DeBoer, and J. Takats, *J. Am. Chem. Soc.*, **93**, 3592 (1971).
- (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.² 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.⁹ The structure was solved by the straightforward application of standard heavy-atom techniques.
- (9) J. L. Atwood, W. E. Hunter, D. C. Hrnrcr, E. Samuel, H. Alt, and M. D. Rausch, *Inorg. Chem.*, **14**, 1757 (1975).
- (10) J. L. Atwood, G. K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, and R. Pearce, *J. Am. Chem. Soc.*, **99**, 6645 (1977).
- (11) J. L. Atwood and W. E. Hunter, unpublished results.
- (12) J. H. Burns, *J. Organomet. Chem.*, **69**, 225 (1974).
- (13) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 2nd ed, Wiley-Interscience, New York, N.Y., 1966, p 768.
- (14) J. L. Atwood, M. Tsutsui, N. Ely, and A. E. Gebala, *J. Coord. Chem.*, **5**, 209 (1976).
- (15) J. L. Atwood, C. F. Hains, M. Tsutsui, and A. E. Gebala, *J. Chem. Soc., Chem. Commun.*, 452 (1973).
- (16) F. A. Cotton, *Discuss. Faraday Soc.*, No. 47, 79 (1969); J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **91**, 2528 (1969).

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μ -Carbonyl- μ -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.¹ Later Green made reference to unpublished results by Davison and Wilkinson who found a single high-field hydride resonance 14.9 ppm relative to Me_4Si for both $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ and $\text{HFe}_3(\text{CO})_{11}^-$.² 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 Me_4Si , 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 ~ 3500 and 1640 cm^{-1} and a weak broad ^1H NMR signal around δ_{H} 6.7 ppm (Me_4Si), which are in the range of H_3O^+ or higher aggregates.^{3,4} 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 N_2 through the red solution lead

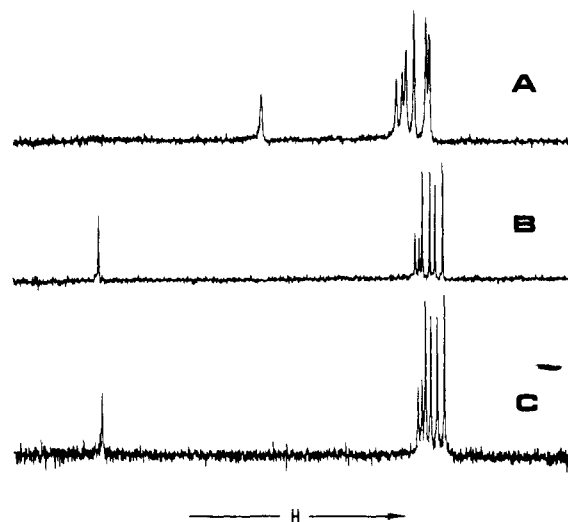
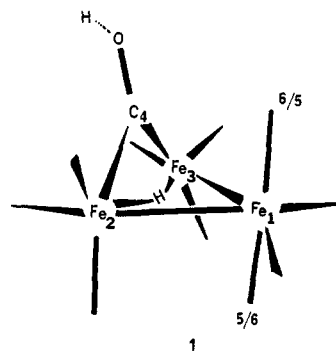


Figure 1. Low-temperature ^{13}C NMR spectra of (A) $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ (-120°C), (B) $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ (-100°C), and (C) $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ (-100°C).

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 CD_2Cl_2 was prepared and cooled to -90°C (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°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**.



^1H NMR spectra of $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ in CD_2Cl_2 were recorded in the range of -80 to -30°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°C an additional proton signal is observed at $\delta 15.0$ ppm, which shifts upfield to $\delta 13.8$ ppm at -40°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 ^1H NMR spectrum of HSO_3F in $\text{CD}_2\text{Cl}_2/\text{Me}_4\text{Si}$ is found at $\delta 10.5$ ppm at -80°C and 10.1 ppm at -40°C .

Further evidence for the nature of $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ was obtained by a comparison of the ^{13}C NMR spectra of $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$,⁵ $\text{H}_2\text{Fe}_3(\text{CO})_{11}$, 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}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}C NMR spectra were recorded in the

range of -100 to -40 °C. In similar experiments the ^{13}C NMR spectra of $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$ were obtained in the range of -120 to 0 °C. At low temperatures, -100 °C for $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ and -120 °C for $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$, both compounds display a 1:1:1:2:2:2:2 pattern in the carbonyl region, which is consistent with the structure of the later in the solid state.⁶ A slight upfield shift is observed for the terminal carbonyl carbons of $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ relative to $\text{HFe}_3(\text{CO})_{11}^-$, but the bridging carbonyl carbon (4) is significantly shifted downfield to δ_{C} 358.78 ppm (Me_4Si) (compared with 283.88 ppm for $[\text{PPN}][\text{HFe}_3(\text{CO})_{11}]$). This shift is similar to the deshielding which results when a bridging carbonyl interacts with a Lewis acid,⁵ and is very close to the ^{13}C resonance for the O-alkylated bridging carbonyl in $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$, δ_{C} 356.9 ppm.

The ^{13}C spectrum of the terminal carbonyl groups for $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ also agrees with the proposed structure. At -100 °C six peaks (217.25, 215.38, 214.00, 210.63, 208.38, and 204.93 ppm) in a 1:1:2:2:2:2 ratio are observed in the terminal carbonyl region of the spectrum. The first two peaks are assigned to the axial carbonyls (5 or 6) on the unique iron atom (1), and the rest are assigned to the equatorial carbonyl carbons on Fe(1) and the three pairs of equivalent carbonyl carbons of Fe(2) and Fe(3).

The proposed structure is confirmed by comparison of the ^{13}C NMR spectra of both $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ and $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$. The later compound is known from x-ray diffraction data⁷ to contain a methyl group attached to a bridging CO ligand. The similarities of the chemical shift and pattern of splitting for $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ and $\text{HFe}_3(\text{CO})_{10}(\text{COCH}_3)$ (Figure 1, B and C) demonstrate that the structures are similar.

There is an interesting contrast between the structures of the isoelectronic pair $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ and $\text{H}_2\text{Os}_3(\text{CO})_{11}$. X-ray analysis⁸ demonstrates that $\text{H}_2\text{Os}_3(\text{CO})_{11}$ contains only metal-bonded hydrogens, one terminal and the other in a two-metal bridging site. The difference in structure between $\text{H}_2\text{Fe}_3(\text{CO})_{11}$ and $\text{H}_2\text{Os}_3(\text{CO})_{11}$ may arise from kinetic factors, because the method of preparation of the osmium cluster⁹ is quite different from that reported here for $\text{H}_2\text{Fe}_3(\text{CO})_{11}$. However, in view of the mobility of H and CO in many clusters, it seems likely that the two different structures represent the thermodynamically stable forms of the respective compounds. The attachment of H^+ to the bridging CO of $\text{HFe}_3(\text{CO})_{11}^-$ is consistent with previous work from our laboratory which demonstrates that bridging carbonyl groups are much more basic than their terminal counterparts.¹⁰ Therefore, one factor which will favor protonation of CO in $\text{HFe}_3(\text{CO})_{11}^-$ is the much greater tendency for the CO ligand to assume a bridging position in a first-row Fe_3 carbonyl rather than in a third-row Os_3 cluster. The viewpoint of acid-base chemistry also leads one to expect that the protonation of Os is favored over protonation of Fe, because third-row transition metal centers are generally more basic than those in the first transition series.¹⁰

One of the earliest proposals for the structure of $\text{H}_2\text{Fe}(\text{CO})_4$ involved the placement of the hydrogens on the carbonyl oxygens,¹¹ but subsequent work consistently has indicated that hydrogen is bound to the central metal in carbonyl hydrides, including $\text{H}_2\text{Fe}(\text{CO})_4$.^{12,13} With the discovery of an O-H linkage in $\text{HFe}_3(\text{CO})_{10}(\text{COH})$ we have come full circle in the description of transition metal carbonyl hydrides. It now becomes necessary to seriously consider the possibility of COH linkages in other metal carbonyl hydrides. Polynuclear carbonyl hydrides are the most likely class of compounds for the occurrence of this type of structure.

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References and Notes

- (1) Hieber, H.; Brendel, G. Z. *Anorg. Allgem. Chem.*, **1957**, 289, 338-344.
- (2) Green, M. L. H. *Angew. Chem.*, **1960**, 72, 719-725.
- (3) Bellamy, L. J. "The Infrared Spectra of Complex Molecule", Vol. 2; Wiley: New York, N.Y., 1975; pp 107-115.
- (4) Gutowsky, H. S.; Saika, A. *J. Chem. Phys.*, **1953**, 21, 1688-1694.
- (5) Wilkinson, J. R.; Todd, L. J. *J. Organomet. Chem.*, **1976**, 118, 199-204.
- (6) Dahl, L. F.; Blount, J. F. *Inorg. Chem.*, **1965**, 4, 1373-1375.
- (7) Shriver, D. F.; Lehman, D.; Strope, D. *J. Am. Chem. Soc.*, **1975**, 97, 1594-1595.
- (8) Churchill, M. R.; Deboer, B. G. *Inorg. Chem.*, **1977**, 16, 878-884.
- (9) Shapley, J. R.; Keister, J. B.; Churchill, M. R.; Deboer, B. G. *J. Am. Chem. Soc.*, **1975**, 97, 4145-4146.
- (10) Shriver, D. F. *J. Organomet. Chem.*, **1975**, 94, 259-271.
- (11) Ewens, R. V. G.; Lister, M. W. *Trans. Faraday Soc.*, **1939**, 35, 681-691.
- (12) McNeill, E. A.; Scholer, F. R. *J. Am. Chem. Soc.*, **1977**, 99, 6243-6249.
- (13) Frenz, B. A.; Ibers, J. A. in "Transition Metal Hydrides", Vol. 1; Muetterties, E. L., Ed.; Marcel Dekker: New York, N.Y., 1971; pp 33-70.

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High Pressure Electron Paramagnetic Resonance Experiments. Effect of Solvent Contraction on Hyperfine Splitting¹

Sir:

There have been very few high pressure EPR experiments and they have all been carried out in specially designed cavities.² In addition, these experiments have tended to concentrate on the effects of pressure on EPR line widths.^{2,3} It seems clear that the full potential of the high pressure technique cannot be explored unless general purpose high pressure vessels are available. Such vessels must be compatible with standard EPR equipment and should allow for photolysis of the samples, since this is the most frequently used procedure for generating transient organic radicals.

Glass tubes have been used successfully in NMR spectrometers at pressures up to 2500 bar.⁴⁻⁷ and we have followed the basic NMR design⁴ to make quartz vessels suitable for EPR use. Heat drawn quartz tubes (3-mm o.d. \times 1-mm i.d.) were further drawn to capillaries at each end. One capillary was cemented into stainless steel pressure tubing, while the other was sealed after introduction of the sample. Pressure was applied with a hand pump and was measured with a Bourdon gauge. Such cells operated to \sim 2000 bar so long as the heat drawn surface remained undamaged. This was achieved by protecting the surface with a layer of light oil. Some 70% of the cells survived testing to 2000 bar and could subsequently be repeatedly pressurized to 1500 bar. Initial experiments were designed to test the effects of solvent contraction on hyperfine splitting.

Temperature-dependent hyperfine splittings have been the subject of frequent study.⁹ The experiments are invariably carried out at *constant pressure*, although it is tacitly assumed when interpreting the data that the systems behave as though they had a *constant volume*. That is, as the temperature is lowered the effects of reducing solvent volume (i.e., increasing solvent density) on the hyperfine splitting have been largely ignored. To test the validity of this assumption we have measured the volume and temperature dependencies of the isotropic nitrogen hyperfine splitting (a^{N}) for di-*tert*-butyl nitroxide in several solvents.

Di-*tert*-butyl nitroxide was chosen because it has been frequently used as a probe in the investigation of radical-solvent interactions.¹⁰⁻¹⁴ In particular, the magnitude of the nitrogen