range of −100 to −40 °C. In similar experiments the ^{13}C NMR spectra of [PPN][HFe$_3$(CO)$_{11}$] were obtained in the range of −120 to 0 °C. At low temperatures, −100 °C for H$_2$Fe$_3$(CO)$_{11}$ and −120 °C for [PPN][HFe$_3$(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 H$_2$Fe$_3$(CO)$_{11}$ relative to HFe$_3$(CO)$_{11}^-$, but the bridging carbonyl carbon (4) is significantly shifted downfield to δ_C 358.78 ppm (Me$_4$Si) (compared with 283.88 ppm for [PPN][HFe$_3$(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 HFe$_3$(CO)$_{10}$(COCH$_3$), δ_C 356.9 ppm.

The ^{13}C spectrum of the terminal carbonyl groups for H$_2$Fe$_3$(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 H$_2$Fe$_3$(CO)$_{11}$ and HFe$_3$(CO)$_{10}$-(COCH$_3$). The later compound is known from x-ray diffraction data[7] to contain a methyl group attached to a bridging CO ligand. The similarities of the chemical shift and pattern of splitting for H$_2$Fe$_3$(CO)$_{11}$ and HFe$_3$(CO)$_{10}$(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 H$_2$Fe$_3$(CO)$_{11}$ and H$_2$Os$_3$(CO)$_{11}$. X-ray analysis[8] demonstrates that H$_2$Os$_3$(CO)$_{11}$ contains only metal-bonded hydrogens, one terminal and the other in a two-metal bridging site. The difference in structure between H$_2$Fe$_3$(CO)$_{11}$ and H$_2$Os$_3$(CO)$_{11}$ may arise from kinetic factors, because the method of preparation of the osmium cluster[9] is quite different from that reported here for H$_2$Fe$_3$(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 HFe$_3$(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 HFe$_3$(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 earlist proposals for the structure of H$_2$Fe(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 H$_2$Fe(CO)$_4$.[12,13] With the discovery of an O–H linkage in HFe$_3$(CO)$_{10}$(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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High Pressure Electron Paramagnetic Resonance Experiments. Effect of Solvent Contraction on Hyperfine Splitting[1]

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 design[4] to make quartz vessels suitable for EPR use. Heat drawn quartz tubes (3-mm o.d. × 1-mm i.d.) were further drawn to capilliaries at each end. One capilliary 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 ~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

Table I. Temperature and Volume Dependencies of a^N for Di-*tert*-butyl Nitroxide

	measd quantities			calcd
	A	B	C	$A - BC$
		$((\partial a^N/$		$((\partial a^N/$
	$((\partial a^N/\partial T)_P)$,	$\partial V)_T)$,	$((\partial V/\partial T)_P)$,	$\partial T)_V)$,
solvent	$G/K \times 10^4$	$G/L \times 10$	$L/K \times 10^3$	$G/K \times 10^4$
cyclo-pentane	-7.7 ± 1.1	-5.1 ± 0.4	1.17	-1.7 ± 1.5
acetone	-15.2 ± 1.5	-6.8 ± 0.8	1.44	-5.4 ± 2.3
ethanol	-6.5 ± 0.8	-7.3 ± 1.0	1.04	1.1 ± 1.8

hyperfine splitting seems to be a sensitive probe of local environment produced by solvent molecules around the solute (the cybotactic region[15]). This is deduced[10,12,13,16] from the fact that the magnitude of a^N in different solvents is best correlated with solvent polarity parameters such as the Kosower Z value[17] and the Dimroth-Reichardt E_T value[18] which are based upon model chemical reactions. By contrast, only poor correlations are obtained[13] with bulk parameters such as dielectric constant.

We can describe a^N for di-*tert*-butyl nitroxide as a function of the pressure, volume, and temperature of the solvent. Since a knowledge of any two of P, V, and T is sufficient to define the third, then the following equation holds:[19]

$$(\partial a^N/\partial T)_P = (\partial a^N/\partial T)_V + (\partial a^N/\partial V)_T(\partial V/\partial T)_P$$

Measurements[20] were carried out for di-*tert*-butyl nitroxide (10^{-3} M) in cyclopentane, acetone, and ethanol, these being regarded as typical of nonpolar, polar, and hydrogen-bonding solvents. For each solvent $(\partial a^N/\partial T)_P$ was measured in a standard variable-temperature experiment at 1 bar over the temperature range of ~40 to -80 °C. Similarly, $(\partial a^N/\partial V)_T$ was obtained by measuring the change in a^N with pressure (range, 1–1400 bar) at 23 °C, which was then converted to a volume change using the known compressions of the solvents.[22] For acetone and ethanol $(\partial V/\partial T)_P$ at 1 bar was obtained from literature data[23] and for cyclopentane it was measured directly. Graphs of a^N vs. volume or temperature were straight lines to within experimental error. The results are summarized in Table I and are available in detailed form as supplementary material. The error limits represent one standard deviation derived from least-squares fitting of the data. The various slopes refer to a point where $P = 1$ bar, $V = 1$ L, and $T = 23$ °C.

As stated previously, the temperature dependence of hyperfine splitting is generally studied at *constant pressure*. It is assumed that the systems behave as though they had a *constant volume*; i.e., it is assumed that $(\partial a^N/\partial T)_P = (\partial a^N/\partial T)_V$. This assumption is incorrect. For di-*tert*-butyl nitroxide in cyclopentane and ethanol *all of the change in hyperfine with temperature is due to change in the volume of the solvent; there is no intrinsic change with temperature at constant volume.* Only for acetone does the system reveal a genuine temperature dependence of the hyperfine. However, this temperature dependence is so small that we prefer not to speculate as to its origin at the present time.

The interpretation of small changes in hyperfine splittings with temperature is a currently popular form of EPR spectroscopy. It is recommended that this activity should not be attempted without careful consideration of radical-solvent interactions.[24,26]

Supplementary Material Available: Listings of a^N and g for di-*tert*-butyl nitroxide as a function of temperature and volume in acetone, cyclopentane, and ethanol solvents (9 pages). Ordering information is given on any current masthead page.

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Rate of Primary Photoproduct Formation for Aqueous Tris(ethylenediamine)chromium(III)

Sir:

We report here what we believe to be the first direct measurement of the rate of primary photoproduct formation for a Cr(III) coordination compound. The experiment is one of monitoring the rate of absorbance change, following excitation at 530 nm by a high intensity, 20-ns laser pulse.[1]

Aqueous $Cr(en)_3^{3+}$ (at pH 2) was chosen as the initial system because of the wealth of other information available. The photochemistry has been studied in detail;[2] aquation occurs with quantum yield $\phi = 0.37$ around 25 °C, the primary product being $Cr(en)_2(enH)(H_2O)^{4+}$.[3] Emission from the first thexi doublet state, $D_1{}^\circ$, has been observed[4] and its lifetime