Eu(dpm)₃–solute mole ratios of 0.4:0.7. Pmr spectra were also obtained on 10% solutions of 1 and 2 in carbon tetrachloride at 220[16] and 300 MHz,[16] respectively.

The aromatic protons of both 1 and 2 appear as singlets at 60 MHz in the absence of Eu(dpm)₃, thus making it impossible to determine the aromatic coupling constants. In the presence of Eu(dpm)₃, the aromatic protons of 1 appear as an AA′XX′ pattern and the aromatic protons of 2 appear as an AMXY pattern. Under high-field strength conditions, the aromatic protons of 1 show an AA′BB′ pattern and the aromatic protons of 2 show an ABCD pattern. All spectra were analyzed by best fit iterative computer analysis using the LAOCN3 program.[17] Eu(dpm)₃-shifted spectra gave good computer fits but were not perfect due to slightly broadened and asymmetric peaks. The coupling constants did not vary more than ±0.05 Hz for the Eu(dpm)₃–solute mole ratios used. Spectra obtained at 220 (1) and 300 MHz (2) gave very good computer fits. Coupling constants obtained from the Eu(dpm)₃-shifted spectra are good to at least ±0.5 Hz while those obtained from the 220- and 300-MHz spectra are good to at least ±0.1 Hz.[18] The results are shown in Table I.

Table I. Coupling Constant Values Obtained for 1 and 2
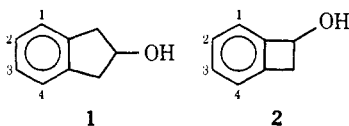
		1		2	
J_{12}	7.29	7.88	6.56	7.45
J_{13}	1.08	1.26	1.28	0.80
J_{14}	0.04	0.11	−0.39	1.87
J_{23}	7.22	7.68	8.35	7.56
J_{24}	1.08	1.26	0.60	0.37
J_{34}	7.29	7.88	7.01	7.59
Rms	0.13	0.05	0.17	0.05
Method	Eu(dpm)₃	220 MHz	Eu(dpm)₃	300 MHz

Statistical analysis of the data reported in Table I using the "t" test method[19] allows several statements concerning comparisons of coupling constants obtained from the Eu(dpm)₃-shifted spectra with coupling constants obtained from the spectra determined at 220 and 300 MHz. The confidence in our results is greater than 99%. In both unstrained[20] 1 and strained[20] 2 the ortho (J_{12}, J_{23}, J_{34}) and para (J_{14} in 2) coupling constants are *not* within experimental error. Thus, coupling constants obtained from Eu(dpm)₃-shifted spectra can be affected by the shift reagent and erroneous

(16) These spectra were recorded by the Varian NMR applications laboratory, Palo Alto, Calif. The probe temperature was 35°.

(17) S. Castellano and A. A. Bothner-By, *J. Chem. Phys.*, **41**, 3863 (1964).

(18) The error is obtained by multiplying the parameter set error[17] by 5 as suggested by S. Castellano, C. Sun, and R. Kostelnik, *Tetrahedron Lett.*, 5205 (1967). M. A. Cooper and S. L. Mannatt (*J. Amer. Chem. Soc.*, **91**, 6325 (1969)) have shown that the error may be better than that obtained by multiplying the parameter set error by 5. Our statistically determined confidence level (99%) would be increased if the multiplication were omitted.

(19) W. J. Youden, "Statistical Methods for Chemists," Wiley, New York, N. Y., 1951, p 24.

(20) M. A. Cooper and S. L. Mannatt, *J. Amer. Chem. Soc.*, **92**, 1605 (1970).

results obtained.[21,23] We therefore suggest that conclusions about aromatic electronic structure based on coupling constants obtained from Eu(dpm)₃-shifted spectra may not be reliable in some cases. A pertinent example for the present work is the study by Cooper and Mannatt[20] who have found that J_{14} increases substantially in benzocycloalkenes on going from large to small cyclic fused rings. This is not observed in the Eu(dpm)₃-shifted spectra.

(21) The *J* values obtained for 1 at 220 MHz and 2 at 300 MHz are considered to be correct due to their near identity with the *J* values reported for benzocyclopentene and benzocyclobutene.[20] Our slightly higher *J* (ortho) values are consistent with the electronegative influence of the –OH group as reported by S. Castellano and C. Sun, *ibid.*, **88**, 4741 (1966). The invariance of *J* with respect to the field strength is well established,[22] thus making comparisons of coupling constants obtained at 60 MHz with coupling constants obtained at high-field strengths valid.

(22) J. W. Emsley, J. Feeney, and L. H. Sutcliff, "High Resolution Nuclear Magnetic Resonance Spectroscopy," Vol. 1, Pergamon Press, Elmsford, N. Y., 1965, Chapter 3, and references cited therein.

(23) Proof that the coupling constant differences observed in the present work are not due to the fact that observations were carried out on different instruments (as suggested by the referees) comes from two sources. (a) The aliphatic ring coupling constants could be extracted directly from the spectra of 1 and 2 in the absence of shift reagent on all spectrometers used. These *J* values were exactly the same regardless of the spectrometer used. (b) L. F. Johnson (*Anal. Chem.*, **43**, 28A (1971)) has shown that coupling constants do not change for acrylonitrile using different spectrometers operating at 60, 100, and 220 MHz.

(23a) Note Added in Proof. B. L. Shapiro, M. D. Johnston, Jr., and R. L. R. Towns (*J. Amer. Chem. Soc.*, **94**, 4381 (1972)) have recently noted lanthanide-induced changes of coupling constants in some ketones.

(24) Research submitted for the degree of Master of Science.

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Proton-Enhanced Nuclear Induction Spectroscopy. Silicon-29 Chemical Shielding Anisotropy in Some Organosilicon Compounds

Sir:

Nmr spectroscopy of ²⁹Si is made relatively difficult both by relatively low isotopic abundance (4.7%) and by the long spin–lattice relaxation times T_1 characteristic of this species. Both of these difficulties are largely circumvented by a double resonance technique[1] in which the rare spins derive an enhanced and rapidly repeatable polarization from abundant spins (protons) by a rotating-frame cross-relaxation process. The experiment is performed in the solid state and therefore affords the possibility of observing anisotropies in the interactions of the rare spins. In many cases the anisotropy of interest is that of the chemical shift; the dipolar broadening by the abundant spins which would otherwise obscure this is then removed by spin decoupling.[1,2]

Table I gives the principle elements of the ²⁹Si chemical shielding tensor obtained by the cross-polarization procedure in polycrystalline samples of a number of organosilicon compounds at −186°. The static

(1) A. Pines, M. G. Gibby, and J. S. Waugh, *J. Chem. Phys.*, **56**, 1776 (1972).

(2) L. R. Sarles and R. M. Cotts, *Phys. Rev.*, **111**, 853 (1958).

Table I. ^{29}Si Chemical Shielding Parameters in Organosilicon Compounds^a

Compound	σ_{11}	σ_{22}	σ_{33}	$\bar{\sigma}$	σ_i
(CH$_3$)$_4$Si	0	0	0	0	0
(CH$_3$)$_3$SiOCH$_3$	−33	−31	8	−19	−17
(CH$_3$)$_2$Si(OCH$_3$)$_2$	−12	−12	35	4	2.5
CH$_3$Si(OCH$_3$)$_3$	23	35	68	42	41.5
Si(OCH$_3$)$_4$	80	80	80	80	79.5
[(CH$_3$)$_3$Si]$_3$CH	−8	4	18	5	
(CH$_3$)$_3$SiC$_6$H$_5$	−2	4	29	10	4.5
[(CH$_3$)$_3$Si]$_2$O	−16	−8	14	−3	−4
[(CH$_3$)$_2$SiO]$_3$	−8	0	62	18	10^b
[(CH$_3$)$_2$SiO]$_4$	4	4	53	20	20

^{a} All values are in parts per million (± 3) relative to solid TMS. $\bar{\sigma} = \frac{1}{3}(\sigma_{11} + \sigma_{22} + \sigma_{33})$. σ_i is the isotropic shift in the neat liquid, referred to liquid TMS (ref 3). ^{b} Solution in C$_6$H$_6$.

field H_0 was 22,800 G, the proton decoupling field H_1 (H) was $\sim$8 G, and the cross-polarization field H_1 (Si) was $\sim$40 G. Each spectrum was obtained in $\sim$10 min of running time using $\sim$200 mg of sample material. All values are referred to an external reference of (solid) TMS. The following points can be made about these values.

(a) The range of ^{29}Si anisotropies, like the range of isotropic ^{29}Si shifts in liquids,[3] is smaller than the corresponding range of ^{13}C values.[4]

(b) With a few exceptions (believed real) the mean shift does not change appreciably on melting. Similar behavior, including exceptions, has been observed previously for ^{13}C.[3]

(c) Deviations from axial symmetry of the shielding tensor arising from crystalline environment are sometimes seen [cf. CH$_3$Si(OCH$_3$)$_3$] in cases where the shielding tensor for the isolated molecule would be expected to be axial.

(d) Since these measurements are made in powders, the orientations of the principal axes in the molecular frame are not known and presumably change from compound to compound. Single-crystal studies would remove this ambiguity.

(3) (a) G. R. Holzman, P. C. Lauterbur, J. H. Anderson, and W. Koth, J. Chem. Phys., 25, 172 (1956); (b) B. K. Hunter and L. W. Reeves, Can. J. Chem., 46 (8), 1399 (1968).
(4) A. Pines, M. G. Gibby, and J. S. Waugh, Chem. Phys. Lett., in press.

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Synthesis and X-Ray Structure of Di-μ-hydrido-octacarbonyldirhenium

Sir:

The first reported polynuclear carbonyl hydride of rhenium was H$_3$Re$_3$(CO)$_{12}$,[1] i.e., [HRe(CO)$_4$]$_3$, in which the hydrogens are considered to bridge the edges of a triangular arrangement of rhenium atoms. We now describe a new dimeric complex H$_2$Re$_2$(CO)$_8$, i.e.,

(1) D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, J. Amer. Chem. Soc., 86, 4841 (1964).

[HRe(CO)$_4$]$_2$, which formally bears the same relation to the trimer as ethylene does to cyclopropane. It is, moreover, the analog of the well-known tetracarbonyl halide dimers of rhenium,[2] although the bonding in the hydride is less readily described in simple terms.

A sample of Ph$_2$SiH$_2$Re$_2$(CO)$_8$[3] (1.0 g) was stirred in chloroform (50 ml) with silicic acid (5 g) for 1 hr. The mixture was filtered and the filtrate evaporated to leave a yellow solid which afforded yellow crystals of H$_2$-Re$_2$(CO)$_8$[4] (0.60 g, 78%) upon recrystallization from dichloromethane–n-hexane at $-20°$. The compound is moderately air stable, darkens above 115°, and decomposes slowly in light. The infrared spectrum exhibits bands assigned to carbonyl stretching modes (see below) at 2093 (3.5), 2020 (10.0), 2000 (8.6), and 1979 (9.8) cm^{-1} (cyclohexane, relative intensities in parentheses). A single sharp proton resonance was observed at τ 19.04 (CDCl$_3$) and shown to be due to two hydrogens using a known molar ratio of Ph$_2$SiH$_2$Re$_2$-(CO)$_8$ as standard. An intense peak due to the molecular ion occurred in the mass spectrum, while peaks due to [HRe$_x$(CO)$_8$]$^+$ or [Re$_2$(CO)$_8$]$^+$ were not observed;[5] this characteristic is indicative of bridging positions for the hydrogens.[6]

No infrared bands that could be attributed to terminal Re–H or Re–D vibrations were observed in cyclohexane solution for H$_2$Re$_2$(CO)$_8$ in the 2200–1800-cm^{-1} region, nor for D$_2$Re$_2$(CO)$_8$ in the 1600–1200-cm^{-1} region. However, the Raman spectrum of the hydride showed bands at 1382 and 1272 cm^{-1}, shifting to 974 and 924 cm^{-1} in the deuteride, and this may be taken as an unequivocal demonstration of bridging positions for hydrogen.[7]

The compound crystallizes as prisms in the monoclinic crystal system with space group $P2_1/c$; lattice parameters $a = 8.96$ (2) Å, $b = 11.62$ (2) Å, $c = 12.85$ (2) Å, and $\beta = 109.2$ (1)°; four molecules per unit cell; $\rho_{obsd} = 3.16$ g/ml (by flotation) and $\rho_{calcd} = 3.18$ g/ml. The crystals decompose in the X-ray beam. This feature, coupled with the relatively large absorption effects (typically transmission factors ranged from 0.1 to 0.2 for the crystals used), severely limited the accuracy of the study. Intensity data were collected from two crystals (dimensions 0.14 × 0.11 × 0.14 mm and 0.12 × 0.13 × 0.10 mm) on a PAILRED diffractometer ($h0l$ to $h12l$) using molybdenum Kα X-radiation that

(2) E. W. Abel, G. B. Hargreaves, and G. Wilkinson, J. Chem. Soc., 3149 (1958); M. A. El-Sayed and H. D. Kaesz, Inorg. Chem., 2, 158 (1963).
(3) J. K. Hoyano, M. Elder, and W. A. G. Graham, J. Amer. Chem. Soc., 91, 4568 (1969).
(4) Anal. Calcd for C$_8$H$_2$O$_8$Re$_2$: C, 16.06; H, 0.34; O, 21.39. Found: C, 16.17; H, 0.45; O, 21.50.
(5) The computed multiplet pattern for [H$_2$Re$_2$(CO)$_8$]$^+$ is (nominal mass, relative abundance) 596 (29.3), 597 (2.7), 598 (100.0), 599 (9.3), 600 (86.4), 601 (8.0), 602 (1.4). The observed pattern was in excellent agreement, with no peaks at 594 or 595 which would have indicated hydrogen loss. Further confirmation of the identity of the compound was provided by an exact mass measurement on the nominal 600 peak. Calculated intensity-weighted mean m/e for all isotope combinations contributing to the nominal 600 peak of H$_2$Re$_2$(CO)$_8$: 599.8869. Found: 599.8860.
(6) J. M. Smith, K. Mehner, and H. D. Kaesz, J. Amer. Chem. Soc., 89, 1759 (1967); B. F. G. Johnson, J. Lewis, and P. W. Robinson, J. Chem. Soc. A, 1684 (1970).
(7) We are grateful to Professor H. D. Kaesz for recording the Raman spectra of these compounds. A detailed study of the Raman modes of these and other hydrogen-bridged systems is in progress in Professor Kaesz's laboratory. Cf. H. D. Kaesz and S. W. Kirtley, Abstracts, 163rd National Meeting of the American Chemical Society, Boston, Mass., April, 1972, No. INOR 131.