in the bulb with liquid nitrogen. The salt (22.5 g) was heated to 90° and the liquid nitrogen was lowered from the bulb and replaced by a water bath at room temperature which forced the disilane to vaporize into the reaction zone. After 1 min, the volatile fraction now contained disilane (0.81 mmole) and 0.74 mmole of chlorodisilane (the proton nmr spectrum of the neat sample consisted of absorptions at −2.82 ppm (SiH_3) and at −4.26 ppm (SiH_2) with relative intensities of 3.0:1.9). The neat sample also contained dichlorosilane (4%) and chlorosilane (2%). Also present in the volatile fraction were more highly substituted chlorodisilanes (0.13 mmole), hydrogen chloride (0.86 mmole), and hydrogen (0.5 mmole).

(3) **CH_3SiH_3–AgCl Reaction.**—The methylsilane was distilled through 22.5 g of silver chloride heated to 260° and condensed in the bulb with liquid nitrogen. The dewar was removed and the methylsilane was allowed to vaporize into the heated zone. About 1 min later, the volatile fraction was condensed at −196° in the vacuum system and analyzed. When 2.17 mmoles of methylsilane reacted with 22.5 g of silver chloride, the volatile fraction contained methylsilane (0.64 mmole), methylchlorosilane (1.31 mmoles), methyldichlorosilane (0.17 mmole), hydrogen chloride (1.61 mmoles), and hydrogen (0.2 mmole). The proton nmr spectrum of the neat methylchlorosilane had a triplet at +1.03 ppm (CH_3) and a poorly defined quartet at −3.13 ppm (SiH_2) of relative intensities 3.0:2.1.

(4) **$(CH_3)_2SiH_2$–AgCl Reaction.**—The reaction between dimethylsilane and silver chloride was carried out as described for the reaction with methylsilane except that the dimethylsilane was exposed to the heated salt for 1 hr. When 1.30 mmoles of dimethylsilane was allowed to react with 22.5 g of silver chloride, the final volatile fraction contained dimethylsilane (0.46 mmole), dimethylchlorosilane (0.48 mmole), dimethyldichlorosilane (0.24 mmole), hydrogen chloride (0.89 mmole), and hydrogen (0.2 mmole). The proton nmr spectrum of the neat dimethylchlorosilane had absorptions at +0.30 ppm (2 CH_3) and at −4.04 ppm (SiH) of relative intensities 6.0:0.9.

(5) **$(CH_3)_3SiH$–AgCl Reaction.**—Trimethylsilane (1.34 mmoles) was allowed to react with silver chloride at 280°. For this reaction the procedure was identical with that for methylsilane except that the trimethylsilane remained exposed to the heated silver chloride for 1.75 hr. After the reaction, the volatile fraction contained trimethylsilane (0.52 mmole), trimethylchlorosilane (0.58 mmole), hydrogen chloride (0.65 mmole), and hydrogen (0.2 mmole).

(6) **SiH_4–AgBr Reaction.**—The reaction between silane and silver bromide was carried out as described in section 4 (1 hr). When 1.30 mmoles of silane was allowed to react with 25 g of silver bromide the volatile products were bromosilane (0.41 mmole), dibromosilane (0.04 mmole), hydrogen bromide (0.02 mmole), and hydrogen (0.5 mmole), while 0.77 mmole of silane was recovered.

Discussion

These reactions can be represented by the following general equations

$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{H} + 2\mathrm{AgCl} \longrightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{Cl} + \mathrm{HCl} + 2\mathrm{Ag} \qquad (1)$$

$$-\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{H} + \mathrm{AgBr} \longrightarrow -\underset{|}{\overset{|}{\mathrm{Si}}}-\mathrm{Br} + {}^1/_2\,\mathrm{H_2} + \mathrm{Ag} \qquad (2)$$

We feel that this method is probably the best general method for the stepwise halogenation of the volatile silicon hydrides. We are currently extending this method to obtain and isolate the chlorodisilanes ($Si_2H_{6-x}Cl_x$ with x = 2–5).

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The Raman Spectra of Manganese and Rhenium Carbonyl Hydrides and Some Related Species

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In the determination of the manganese–hydrogen bond length of $HMn(CO)_5$ from the second moment of the broad line proton magnetic resonance spectrum,[1] it was necessary initially to assume that the hydrogen atom was located on the C_4 axis of the presumably C_{4v} molecule.[2] In view of our subsequent treatment of this and other carbonyl hydrides as effectively isolated two-spin systems,[3] this assumption was no longer necessary to establish the metal–hydrogen distance. We have therefore studied the Raman spectrum of this and several related molecules in an attempt to establish, in the absence of any direct information, the orientation of the hydrogen atom. The infrared spectral evidence for the structure is confused by C^{13}, overtone, and combination bands[4] in solution and in addition by pqr structure in the gas phase.[5]

The spectra (Figure 1 and Table I) and, in particular, the polarizations are consistent with C_{4v} symmetry for both manganese and rhenium carbonyl hydrides. The following points concerning the spectra are noteworthy. (1) The metal–hydrogen stretching mode is particularly intense, indicating a large polarizability change during vibration. A significant polarization indicates that it is a totally symmetric mode and presumably that the hydrogen is on the fourfold axis. (2) The polarization of the high-energy band shows that this also is a totally symmetric mode confirming the assignments previously made from the infrared spectra.[4] (3) The spectra of the neat liquids show considerable shifts from the position of the frequencies expected on the basis of infrared spectra taken in hydrocarbon solvents. (4) The relative intensities and the positions of the bands are markedly dependent on the nature of the metal and the X group in the $XM(CO)_5$ systems. (5) The resolution of five bands in crystalline $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ represents some activation of infrared bands in the crystal, but nevertheless is consistent with the previous assignments.[6] (6) The spectrum of solid

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[1] T. C. Farrar, W. Ryan, A. Davison, and J. W. Faller, *J. Am. Chem. Soc.*, **88**, 184 (1966).

[2] The $Mn(CO)_5$ moiety has been shown to have essentially C_{4v} symmetry in crystalline $HMn(CO)_5$: S. J. LaPlaca, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1495 (1964).

[3] T. C. Farrar, F. E. Brinkman, T. D. Coyle, A. Davison, and J. W. Faller, *ibid.*, **6**, 161 (1967).

[4] D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

[5] (a) F. A. Cotton, J. L. Down, and G. Wilkinson, *J. Chem. Soc.*, 833 (1959); (b) W. E. Wilson, *Z. Naturforsch.*, **13b**, 349 (1958).

[6] (a) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, **4**, 1328 (1965); (b) J. Lewis, A. R. Manning, J. R. Miller, and M. J. Ware, *Nature*, **207**, 142 (1965).

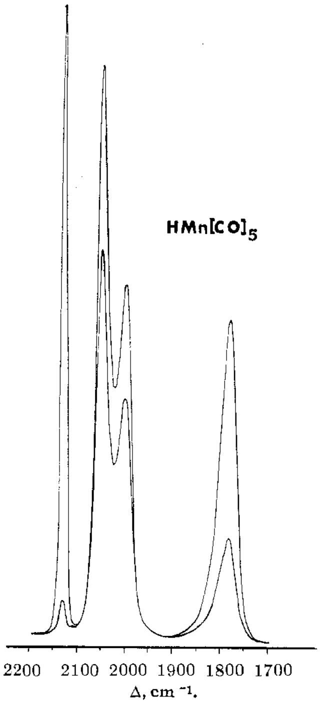

Figure 1.—The Raman spectrum of $HMn(CO)_5$; the upper trace is the spectrum with parallel polarization, and the lower is that with perpendicular polarization.

TABLE I

THE PRINCIPAL LINES IN THE RAMAN SPECTRUM OF $HMn(CO)_5$ AND $HRe(CO)_5$

		$HMn(CO)_5$			$HRe(CO)_5$		
Assignment[a]		$\Delta\tilde{\nu}$, cm^{-1}	$\Delta\tilde{\nu}_{1/2}$,[b] cm^{-1}	ρ	$\Delta\tilde{\nu}$, cm^{-1}	$\Delta\tilde{\nu}_{1/2}$,[b] cm^{-1}	ρ
$A_1^{(2)}$	$\nu_{CO_{eq}}$	2119	12	0.05	2133	10	0.08
B_1	ν_{CO}	2041	30	0.67	2050	22	0.83
E	ν_{CO}						
		1993[c]	34	0.65	1994[c]	36	0.84
$A_1^{(1)}$	ν_{CO}						
A_1	ν_{MH}	1780	39	0.32	1824	37	0.51
	δ_{CO}, δ_{CM}	403	12		450	17	

[a] The symmetry of the normal coordinates and the primary contribution motions are listed as previously defined by Cotton, *et al.* [ref 6a; F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962)]. [b] The width at half-height. [c] Not resolved. See Experimental Section.

$BrMn(CO)_5$ shows clearly the four modes expected for a C_{4v} molecule.

Comparison of the Raman values for $Mn_2(CO)_{10}$ with those predicted from infrared overtone spectra[6] particularly points out the caution which must be exercised in using overtones, as well as different phases, when calculating frequencies, for errors of 10–15 cm^{-1} are common (this magnitude of error was acknowledged by the previous workers[6]). This is not meant to imply

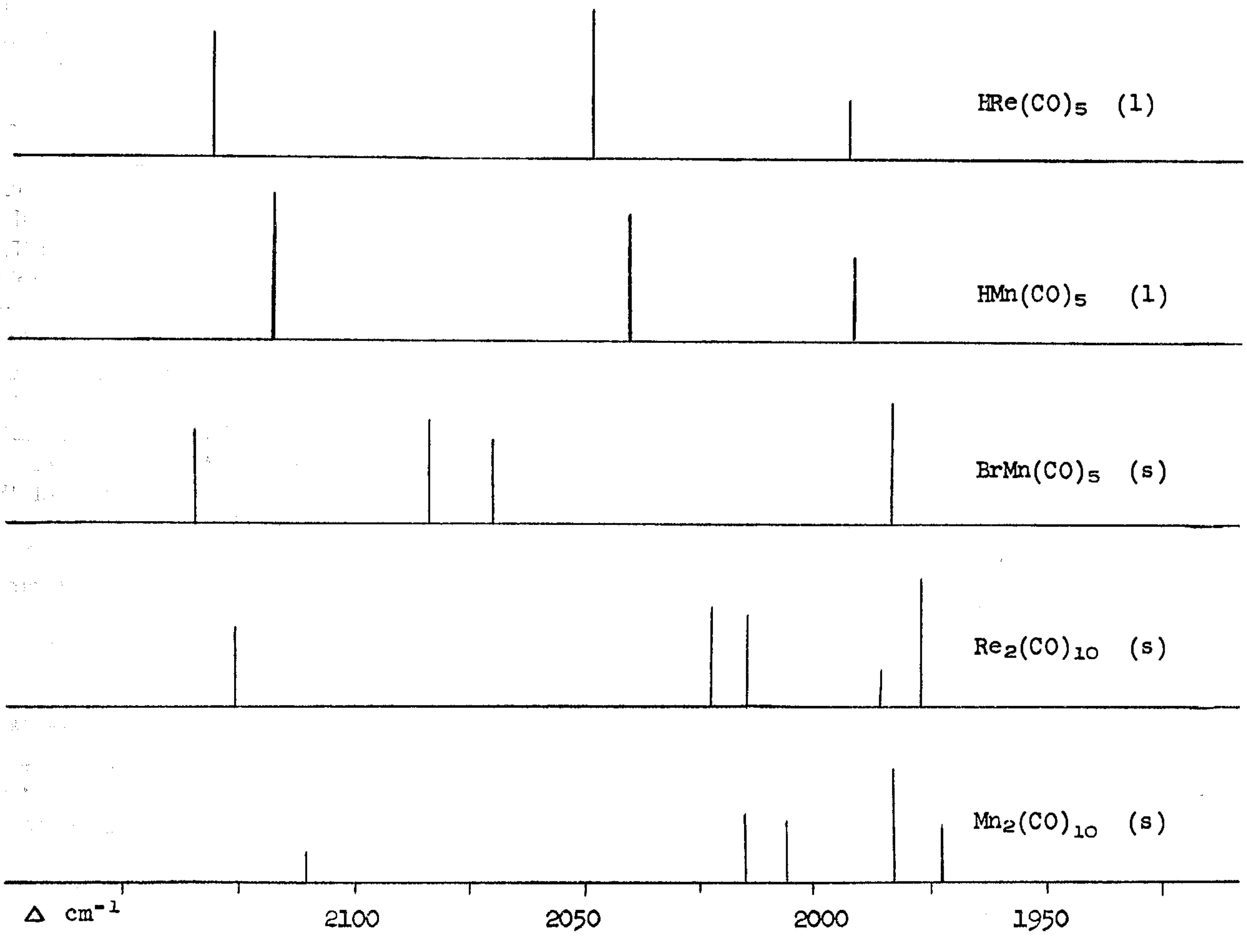

Figure 2.—A comparison of Raman-active carbonyl stretching frequencies.

that overtone arguments should be disregarded, only that overtones can presumably best be used when they are sufficiently well separated that accidental degeneracies do not restrict their value and the limitations are fully appreciated.

Experimental Section

Preparation of Compounds.—The carbonyls $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from Alfa Inorganics but were recrystallized from toluene and sublimed prior to use. The hydrides $HMn(CO)_5$ and $HRe(CO)_5$ were prepared by the acidification of the corresponding sodium pentacarbonylmetalate, which had first been heated at 60° *in vacuo* (0.01 mm) for 72 hr. They were carefully dried by repeated bulb-to-bulb distillations onto P_4O_{10}. Several further distillations were carried out to remove traces of P_4O_{10} which distils slowly under high vacuum. No traces of any impurities could be found in the pure samples of the colorless hydrides in the microwave, mass, or nmr spectra.[7] The $BrMn(CO)_5$ was made by the procedure of Abel and Wilkinson.[10]

Physical Measurements.—The spectra were obtained on a Perkin Elmer LR-1 equipped with a helium–neon laser and a Cary Model 81 with Hg 4358 A excitation. The accuracy of the Raman lines is believed to be ± 3 cm^{-1}. The polarizations were obtained on the LR-1, since the laser presents an inherently more convenient and accurate arrangement. The use of the red line laser excitation is particularly valuable with $Mn_2(CO)_{10}$ and $BrMn(CO)_5$ because of their color. The use of the Toronto arc with $HMn(CO)_5$ was particularly inconvenient due to free-radical decomposition induced by the radiation.[11] The carbonyl hydrides were run as neat liquids, the others as solids. The assignments of the principal lines in the carbonyl hydride spectra are listed in Table I. No corrections were made for instrument polarization. However, the depolarization ratios are relatively accurate for $HMn(CO)_5$ (on this instrument the value of 0.007 for the A_1 mode of CCl_4 is very close to that predicted). A 0.25-ml microcell was used for the $HRe(CO)_5$ measurements; hence, reflections tend to give high values of ρ (this presumably accounts for the observation that ρ_1 is greater than 0.75). The values for the B_1 and E modes are probably within the experimental error; however, a portion of their polarization is very likely due to the A_1 mode beneath them. Presumably the $A_1^{(1)}$ mode is weak and buried under the B_1 and E modes; a shoulder is observed at 2031 cm^{-1} in $HRe(CO)_5$ which may be due to this vibration.[13] The relative intensities of the lines in the other spectra are given in Figure 2. The numerical values for the Raman lines (in cm^{-1}) are: $BrMn(CO)_5$, 1984, 2072, 2086, 2137; $Mn_2(CO)_{10}$, 1973, 1984, 2007, 2017, 2112; $Re_2(CO)_{10}$, 1977, 1985, 2015, 2024, 2126.

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(7) The microwave spectra were determined using both a conventional Stark modulated spectrometer and a Hewlett-Packard phase-stabilized Model 8400 X-band spectrometer capable of sensitivities of 5×10^{-10}/cm. THF has an intense microwave spectrum and preliminary drying of the sodium carbonylmetalates must be carried out for 72 hr or more to avoid contamination with THF. The absence of the THF lines in the microwave spectrum of the samples indicates essentially complete removal of this impurity. It was hoped that further information regarding the structure of hydrides would be forthcoming from their microwave spectra. The absence of any detectable spectra, even in the extremely sensitive Hewlett-Packard instrument, indicates that the dipole moment of 0.75 D. calculated by conventional methods[8] is an upper limit. Comparison with the intensity of the spectrum[9] of $C_5H_5Mn(CO)_3$ suggests that the dipole moment is probably less than 0.5 D. (assuming of course that the C_{4v} structure is retained in the gas phase and that some tunneling mechanism is not reducing the effective moment). The mass spectrum gave no indication of THF or P_4O_{10} impurities; however, it does attest to the stability of the manganese–hydrogen bond, for the fragmentation pattern showed consecutive loss of carbon monoxide moieties with a large percentage of the metal-containing fragments retaining the hydrogen.

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(11) Irradiation of the solid at −70° with a Hg arc gives a red coloration to the crystals, which exhibit a six-line esr spectrum presumably due to $(CO)_5Mn\cdot$ (inferred from the mass spectra of $Mn_2(CO)_{10}$).[12]

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(13) The line of $HMn(CO)_5$ at 1993 cm^{-1} is not assigned as the A_1 mode on the basis of polarization; however, the depolarization ratio is not necessarily small in any but cubic point group molecules. Therefore, it might well be that the shoulder at 2031 cm^{-1} in $HRe(CO)_5$ is the E mode and that the 1994 cm^{-1} line in $HRe(CO)_5$ and the 1993 cm^{-1} line in $HMn(CO)_5$ are A_1 modes.

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Proton and Aluminum-27 Nuclear Magnetic Resonance Studies of Aluminum(III) Perchlorate in N,N-Dimethylformamide

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Proton Resonance.—In recent proton nmr studies of N,N-dimethylformamide (DMF) solutions of anhydrous perchlorate salts of transition metal ions, it has been shown that the primary solvation spheres of the cations Ni^{2+},[1] Co^{2+},[1] Cu^{2+},[2] Fe^{3+},[2] and Cr^{3+} [2] are kinetically well defined. Although the solvent molecules in the primary solvation spheres of most diamagnetic cations are apparently too labile to detect by ordinary techniques, isotope dilution[3] and oxygen-17 nmr studies[4,5] of the aqueous solutions of $Al(ClO_4)_3$ have been used to distinguish water in the primary solvation sphere of Al^{3+} from that in the bulk of the solution. A recent report[6] of the determination by proton nmr of the primary solvation number (six) of Al^{3+} in the solvent dimethyl sulfoxide has prompted this communication of our study of the kinetics and stoichiometry of the solvation of the Al^{3+} ion in anhydrous DMF.

At temperatures below 95°, the 100-Mc proton nmr spectra of solutions of $Al(DMF)_6(ClO_4)_3$ in DMF consist of six signals, three of which can be assigned to DMF in the primary coordination sphere of the Al^{3+} ion and three to DMF in the bulk of the solution. The three signals of DMF in each environment consist of a low-field signal due to the formyl proton and two high-field signals due to the nonequivalent N-

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