are shown in Figure 7. The progressive shifts with increasing ^{13}CO substitution are evident, eventually resulting in a spectrum resembling in every way that of the all-^{12}CO molecule, but completely shifted to lower energy for the all-^{13}CO molecule. The 100% ^{13}CO-substituted molecule was not achieved in this work to any significant extent due to availability of only 50% ^{13}C-enriched CO. The spectra of intermediate species show some regions of overlap of peaks but at least some peaks which are essentially unobscured and may be used as characteristic absorptions for the identification of the particular species in question.

Acknowledgment. We wish to thank the Applied Physics Corporation (now Cary Instruments, a Varian subsidiary) in Monrovia, Calif., for making available to us the laser-source Cary 18 Raman spectrophotometer. We also acknowledge the UCLA Computation Facility for making available intramurally supported computer time, and Miss Karen Mehner for preparation of the figures.

Spectroscopic Studies of Isotopically Substituted Metal Carbonyls. II. Assignment of Carbonyl Stretching Absorptions and Their Interaction with Metal–Hydrogen Stretching Modes in Pentacarbonyl Hydrides[1]

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Contribution No. 2007 from the Department of Chemistry, University of California, Los Angeles, California 90024. *Received December 17, 1966*

Abstract: The infrared absorptions for $Mn(CO)_5H$, $Mn(CO)_5D$, $Re(CO)_5H$, and $Re(CO)_5D$ have been recorded in the region 1900–2200 cm^{-1}. All of the observed maxima are accounted for through assignment to the carbonyl stretching modes of the major constituent, $HM(^{12}CO)_5$, and of the principal isotopic species in natural abundance, $HM(^{12}CO)_4{}^{13}CO$, 4% ^{13}CO *cis*, and 1% ^{13}CO *trans* to hydrogen. Calculations of force constants in the energy-factored carbonyl stretching block of the (FG^{-1}) matrix support these assignments. The ^{13}CO absorptions have been experimentally verified through enrichment; axial and radial CO groups are observed to be approximately equally enhanced by ^{13}CO exchange, in agreement with previous radiocarbon tracer studies. A shift in some of the CO absorptions in going from $HRe(CO)_5$ to $DRe(CO)_5$ has been observed. This is due to coupling between Re–H and *trans*-CO group stretching vibrations. An interaction force constant has been calculated by including the Re–H stretching vibration in the energy-factored (FG^{-1}) matrix. These calculations also provide an interesting check on the method of energy-factored vibrational analysis.

Early spectroscopic studies of the pentacarbonyl hydrides of manganese[2] and rhenium[3] were based on the assumption (derived from earlier electron diffraction work)[4a] that the hydrogen in these compounds did not occupy a position on the coordination sphere of the metal. Subsequent structural determinations on more stable molecular hydrides such as $HPtBr(PEt_3)_2$[4b] and $HOsBr(CO)(PPh_3)_3$[4c] revealed that the hydrogen must in fact be counted into the coordination number of the metal like other ligands. At this time, the spectra of the pentacarbonyl halides, especially the extremely low intensity of one of the fundamentals, A_1 (radial), was under study in these laboratories.[5] The realization that the halides and the hydrides might possess related geometry suggested a similar approach to the assignment of spectra in these two series of molecules.[6a] We concluded that the spectra of the hydrides were consistent with an octahedral model in which hydrogen occupied a coordination position around the metal in the hydrides[6a,b] like the halogens in the halides. This was formally proposed[6a] shortly before the crystal structure of $HMn(CO)_5$ was reported.[7a]

We now wish to report complete assignment of carbonyl modes of all the principal species occurring in natural abundance in the pentacarbonyl hydrides: 95% all-^{12}CO, 4% mono-^{13}CO radial, 1% mono-^{13}CO axial. All the absorptions in the spectra of the pentacarbonyl hydrides are thus accounted for, which had confused the earlier infrared structure assignments for these derivatives. The ^{13}CO modes have been experimentally verified through exchange with ^{13}C-enriched CO.

To confirm the previously assigned metal–hydrogen stretching absorptions,[2a,3] we have also repeated the spectra of $DMn(CO)_5$ and $DRe(CO)_5$. In addition to the large shift in the M–H stretching absorptions, we

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(1) (a) Work supported by Grant GP 4175 from the National Science Foundation; (b) for part I of this series, see H. D. Kaesz, R. Bau, D. Hendrickson, and J. M. Smith, *J. Am. Chem. Soc.*, **89**, 2844 (1967).

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

(3) W. Beck, W. Hieber, and G. Braun, *Z. Anorg. Allgem. Chem.*, **308**, 23 (1961).

(4) (a) See references cited by J. A. Ibers, *Ann. Rev. Phys. Chem.*, **16**, 389 (1965); (b) P. G. Owston, J. M. Partridge, and J. M. Rowe, *Acta Cryst.*, **13**, 246 (1960); (c) P. L. Orioli and L. Vaska, *Proc. Chem. Soc.*, 333 (1962).

(5) M. A. El-Sayed and H. D. Kaesz, *J. Mol. Spectry.*, **9**, 310 (1962).

(6) (a) Dissertation, D. K. Huggins, University of California at Los Angeles, Oct 1963, pp 48–68; (b) D. K. Huggins and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 2734 (1964).

(7) (a) Reported by J. A. Ibers, 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April 1964, Paper No. 50; (b) *cf.* S. J. La Placa, J. A. Ibers, and W. C. Hamilton, *J. Am. Chem. Soc.*, **86**, 2288 (1964).

Table I. Infrared Absorptions (cm^{-1}) of Pentacarbonyl Hydrides and Deuterides[a]

	a	b	c	d	e	f	g	h
$HMn(CO)_5$	2116.7	2109.8	$\sim$2042.0[b]	2035.4	2014.5	2006.7	1981.8	1965.4
$DMn(CO)_5$	2117.0	2109.8	$\sim$2044.0	2036.5	2014.7	2005.4	1981.5	1964.4
$HRe(CO)_5$	2131.1	2123.1	2053.2[b]	2042.5	2014.5	2005.3	1982.3	1966.9
$DRe(CO)_5$	2130.8	2122.9	2051.2	2042.8	2014.5	1999.6	1982.1	1958.2

[a] See Figure 1 for identification of these bands according to designated letters. To allow future checks on our calculations, frequencies are given to a precision of one significant figure beyond our actual experimental accuracy (±1 cm^{-1}). [b] This band is assigned as the Raman-active B_1 band; it apppears as a weak band in only the most concentrated solutions; it has been observed directly by laser-excitation Raman of the neat liquids by A. Davison and J. W. Faller, Massachusetts Institute of Technology, private communication: $HMn(CO)_5$, 2047, and $HRe(CO)_5$, 2055 cm^{-1}.

observed for $DRe(CO)_5$ for the first time[8,9] *distinct shifts in at least two of the absorptions in the carbonyl stretching region which were not reported by previous workers.* These shifts permit unambiguous assignment of these carbonyl bands to A_1 modes, the same symmetry species as the M-H stretching vibrations with which these have apparently become mixed.

Experimental Section

Preparation. The pentacarbonyl hydrides and deuterides were prepared by methods previously reported for these derivatives.[10] Some additional details only need be mentioned here. The parent carbonyls, $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$, were purchased from Alfa Inorganics, Beverly, Mass. After reduction of the carbonyls by sodium amalgam in tetrahydrofuran, we found, as others did before, that it is exceedingly difficult to obtain the dry salts necessary in order to get spectroscopically pure hydride derivatives in the acidification step. The impurities in the sticky solids remaining after reduction and 2 days of pumping under high vacuum up to 50° are extracted with cyclohexane which leaves, after drying under reduced pressure, a slightly colored powder as the pentacarbonyl salt.

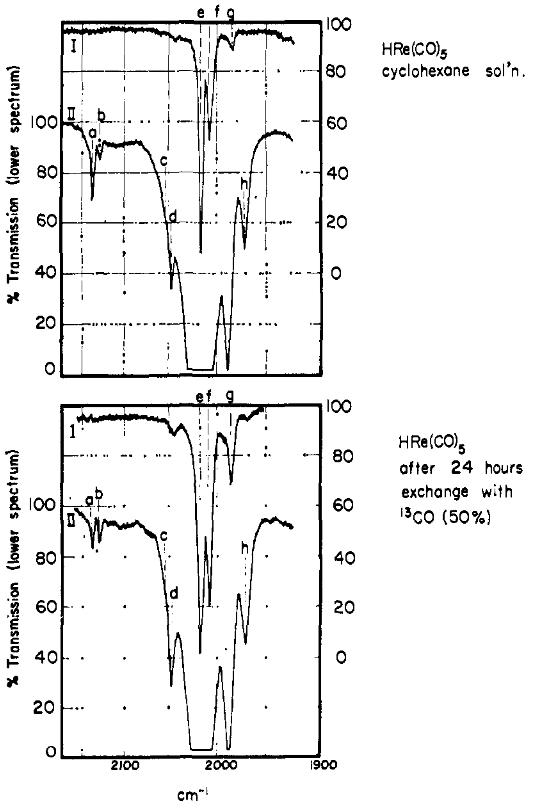

Figure 1. High-resolution infrared absorptions in the carbonyl stretching region for $HRe(CO)_5$ before and after 24-hr exchange with 50% ^{13}C-enriched CO; cyclohexane solution and LiF prism.

The salt is treated under high vacuum with phosphoric acid which has previously been purged with purified nitrogen for several days and then degassed. The volatile products from the acidification are distilled into a trap containing P_4O_{10} and cooled to −196°. After completion of the reaction, cyclohexane is distilled into the trap and further purification of the hydride is accomplished by distilling the solution onto fresh quantities of P_4O_{10} until complete dryness is attained.

The deuterides are prepared using D_3PO_4 in the acidification step. However, care must be taken with the vacuum line as the hydrides will exchange rapidly with any protonic sites on the glassware not removed even by pumping at 10^{-6} mm for prolonged periods. Such equipment may be properly conditioned for this work by exposure to D_2O vapor before exposure to any deuteriometal pentacarbonyls.

The yields of $HRe(CO_5)$ (about 30%) are much lower than for $HMn(CO)_5$ (about 85%). For preparation of hydride sufficient to give the infrared spectra reported here, it was necessary to start with 2.0 g of $NaRe(CO)_5$ but only with 0.5 g of $NaMn(CO)_5$.

A great deal of the rhenium may be found in the product mixture in the form of polynuclear carbonyl hydrides of low volatility, described elsewhere.[8,11]

Exchange Reactions and Infrared Spectra. The procedures have been described in the accompanying publication.[1b] The spectra for $HRe(CO)_5$ at two concentrations are shown in upper spectrum of Figure 1. The absorptions after 24-hr exchange with ^{13}C-enriched CO are shown on the lower spectrum. The positions of the maxima as labeled in the figure are given in Table I.

The spectrum of $DRe(CO)_5$ in the region 1900–2200 cm^{-1} is shown in Figure 2. The vertical dashed lines indicate the position of band f and its ^{13}CO satellite band h in $HRe(CO)_5$, some of which is present in the sample due to imperfect isotopic conversion. The shifts for the two bands f and h are the only perceptible changes in the carbonyl stretching region on going from $HRe(CO)_5$ to $DRe(CO)_5$. No such observable shifts are found for the manganese derivatives. These shifts, if any, must be within the range of experimental error which is 1 cm^{-1} under our present method of operation. The presence of some residual amount of $HRe(CO)_5$ in the $DRe(CO)_5$, shown in Figure 2, is due to exchange of deuteride with traces of water in the apparatus which was used to handle the cyclohexane solution of $DRe(CO)_5$. The last traces of $HRe(CO)_5$ may be removed by shaking the cyclohexane solution with oxygen-free D_2O. Conversely, the $HRe(CO)_5$ may be regenerated simply by shaking the cyclohexane solution with oxygen-free H_2O. Exchange even in such a heterogeneous system is remarkably rapid.

The metal-hydrogen stretching frequencies, although previously reported,[2a,3] have been checked for internal consistency with our present data. The most concentrated solutions of the appropriate derivatives in cyclohexane were scanned with Perkin-Elmer 421 (grating) spectrophotometer. The observed frequencies were found to be as follows: ν_{MnH} 1775, ν_{MnD} 1285, ν_{ReH} 1882, ν_{ReD} 1313 cm^{-1}.

Calculations. Force constants and "normal" modes were calculated using the iterative computer program of Schachtschneider and Snyder[12] described in the accompanying communication.[1b] Calcu-

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[8] D. K. Huggins, W. Fellmann, J. M. Smith, and H. D. Kaesz, *J. Am. Chem. Soc.*, **86**, 4841 (1964).

[9] L. Vaska, *ibid.*, **88**, 4100 (1966).

[10] (a) R. B. King and F. G. A. Stone, *Inorg. Syn.*, **7**, 198 (1963); (b) "Organometallic Syntheses," Vol 1, J. J. Eisch and R. B. King, Ed., Academic Press Inc., New York, N. Y., 1965, pp 158–160.

[11] W. Fellmann and H. D. Kaesz, *Inorg. Nucl. Chem. Letters*, **2**, 63 (1966).

[12] J. H. Schachtschneider and R. G. Snyder, *Spectrochim. Acta*, **19**, 117 (1963).

lations were performed on the IBM 7094 at the UCLA Computation Center.

Discussion

Assignment of Absorptions. The three fundamentals A_1, A_1, and E for $HM(^{12}CO)_5$ are chosen according to methods described in the previous work on the pentacarbonyl halides.[1b] The most intense band, e, will no doubt be the E mode. For the two A_1 modes we choose the weak band at highest energy, a, and a band of medium intensity at lower energy, band f. The assignment of band f as an A_1 species is supported by its observed shift upon deuteration in $DRe(CO)_5$.[8] Only a band of the same symmetry species as the metal–hydrogen stretching modes (which must be of A_1 species) could be affected upon deuteration. No perceptible shift in the position of band a is observed in $DRe(CO)_5$, presumably because this band is less mixed with the Re–H stretching absorption than is band f. Similar discrimination in the interactions of metal hydride with certain carbonyl stretching modes has been reported by Vaska.[9]

There are indications that the weak band at ~2044 cm^{-1}, band c in $HMn(CO)_5$, might be the Raman-active B_1 mode for the C_{4v} molecule. A previous calculation[13a] using the approximate secular equations of Cotton and Kraihanzel indicated that the B_1 mode of that derivative might be expected somewhere in this vicinity (calculated position, 2046 cm^{-1}). This band could gain intensity in the infrared from some breakdown of the C_{4v} symmetry in solution by asymmetric packing of molecules, as suggested by earlier workers in a similar situation for $Mo(CO)_6$.[13b] The computations indicate that the best fit is obtained when this band is indeed attributed to the Raman mode which assignment is finally proved by the failure of this band to gain intensity during ^{13}CO enrichment (see below).

The remaining weak bands may be assigned to either one of the two isotopically substituted species in natural abundance containing one ^{13}CO group, similar to methods outlined previously.[1b] For the axially ^{13}CO-substituted molecule, the E and B_1 but not the A_1 modes will be identical with those for the all-^{12}CO molecule. We assign band h as the A_1 (axial) ^{13}CO mode, which is shifted by 38 cm^{-1} to lower energy from the corresponding ^{12}CO band (f). This is less than the full isotopic shift of 45 cm^{-1} (or more for frequencies uncorrected for anharmonicity).[14] We may thus infer that this mode is mixed with one (or more) other mode of the same symmetry (A_1). The most likely are the A_1 (radial) carbonyl and the A_1 M–H stretching modes. We therefore expect a band slightly shifted to lower energy from band a (the A_1 (radial) band of the all-^{12}CO molecule). It is tempting to assign band b as the A_1 (radial) mode for the ^{13}CO-substituted C_{4v} derivative, but, in fact, such a trial assignment gave a poorer fit by the computer in favor of a band even closer to band a than band b (as discussed below). Such a band has not been resolved by us. It must be pointed out that such a band, belonging to a very weak absorption of a molecule present only in 1% concentration, is probably too weak to be resolved between the already existing bands a and b without specific isotopic substitution. Assignment of the remaining bands is settled through the calculation of force constants.

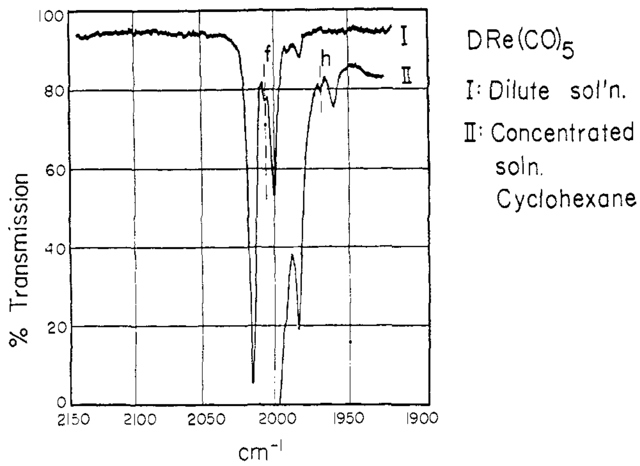

Figure 2. High-resolution infrared absorptions in the carbonyl stretching region for $DRe(CO)_5$ with some $HRe(CO)_5$ present in small quantity as impurity (distinguishing peaks marked with dashed vertical lines).

Calculations. As described above, we feel rather confident about the assignment of bands a, e, f, g, and h. The uncertainty arises for band b (a choice between the A_1 mode for the C_{4v} or for the C_s isotopically substituted molecules) and bands c and d. We may decide the best assignment for these by comparing the calculated values with those observed (which of course are therefore not used as input). The best result is shown in Table II.

Table II. Comparison of Calculated with Observed Frequencies (cm^{-1}) for $DRe(CO)_5$

	Vibr species	Input	Calcd	Obsd	Band	Force constants, mdynes/A
All-^{12}CO (C_{4v})	A_1	2130.8	2130.7	2130.8	a	
	A_1	1999.6	1999.5	1999.6	f	
	B_1	2051.0	2051.0	2051.0	c[a]	
	E	2014.5	2014.4	2014.6	e	
						$K_1 = 16.37$
Mono-^{13}CO (C_{4v})	A_1		2127.1	...[b]		$K_2 = 16.98$
	A_1	1958.2	1958.3	1958.2	h	$K_c' = 0.281$
	B_1		2051.0	...[c]		$K_c = 0.330$
	E		2014.4	...[c]		$K_t = 0.582$
Mono-^{13}CO (C_s)	A′	2122.9	2123.0	2123.1	b	
	A′		2044.1	~2043	d	
	A′		2000.7	...[d]		
	A′	1982.1	1982.2	1982.1	g	
	A″		2014.4	...[c]		

[a] Seen only in very concentrated solutions as a very weak peak; has been measured by laser Raman (at 2055 cm^{-1}) for $HRe(CO)_5$ by A. Davison and J. W. Faller, Massachusetts Institute of Technology, private communication. [b] Probably too weak to be observed between bands a and b. [c] Degenerate with corresponding mode of all-^{12}CO molecule. [d] Obscured by intense absorption of band e.

Similar calculations were carried out for the other molecules studied here and the results are summarized in Table III.

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(13) (a) J. B. Wilford and F. G. A. Stone, *Inorg. Chem.*, **4**, 389 (1965); (b) L. H. Jones, *J. Chem. Phys.*, **36**, 2375 (1962).

(14) Shifts greater than the calculated amount are usually observed in molecules possessing unique CO or NO (using frequencies uncorrected for anharmonicity); see (a) D. P. Tate, J. M. Augl, W. M. Ritchey, B. L. Ross, and J. G. Grasselli, *J. Am. Chem. Soc.*, **86**, 3261 (1964); (b) R. S. McDowell, W. D. Horrocks, and J. T. Yates, *J. Chem. Phys.*, **34**, 530 (1961).

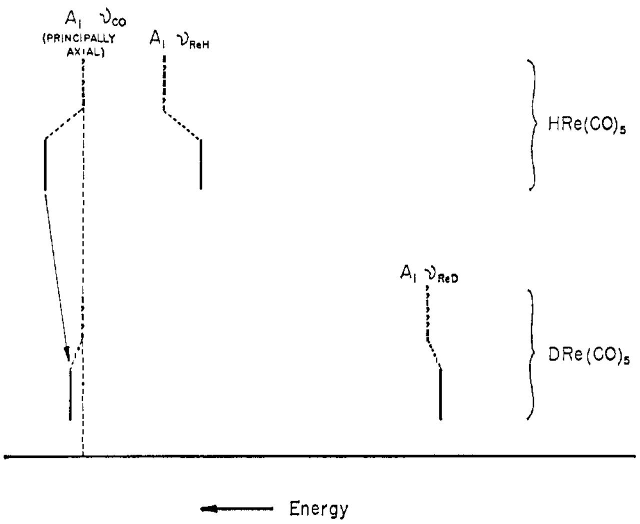

Figure 3. Representation of observed shift (diagonal arrow) of A_1 (principally axial) carbonyl stretching absorption when H is replaced by D in going from $HRe(CO)_5$ to $DRe(CO)_5$. The vertical dashed lines represent the symmetry coordinates before mixing of ν_{CO} with either ν_{ReH} or ν_{ReD}. The solid vertical lines represent the positions of the observed bands.

Interaction of Metal-Hydrogen and Carbonyl Stretching Vibrations. A shift in carbonyl frequencies was first observed by Huggins, Fellmann, Smith, and Kaesz in the pair of derivatives, $H_3Re_3(CO)_{12}$ and $D_3Re_3(CO)_{12}$.[8] This implied a coupling between metal-hydrogen and carbonyl stretching modes, not previously reported for known carbonyl hydrides such as $HMn(CO)_5$ whose deuterium derivatives had also been studied.[2a,3] In our bands, upon repeating this work, we indeed found a shift in the carbonyl frequencies in the pair of compounds $HRe(CO)_5$-$DRe(CO)_5$ (see Experimental Section). No shifts within the limits of our experimental error were noticed for the analogous manganese derivatives, however. Calculations with the rhenium derivatives therefore were carried out in which the metal-hydrogen stretching frequency was included in the energy-factored (FG^{-1}) matrix. In this case, all of the available carbonyl absorptions were placed in their assigned positions (determined by previous successful calculations carried out on the carbonyl modes alone). The results of this calculation are also shown in Table III (fourth row of numbers).

Table III. Summary of Force Constants (mdynes/A)[a,b] for the Best Assignment of Carbonyl Modes in Metal Pentacarbonyl Hydrides and Deuterides

	K_1	K_2	$K_{c'}$	K_c	K_t
$HMn(CO)_5$	16.46	16.88	0.266	0.299	0.480
$DMn(CO)_5$	16.47	16.88	0.257	0.304	0.485
$HRe(CO)_5$	16.60	16.95	0.247	0.391	0.550
$HRe(CO)_5$[c]	16.34	16.96	0.282	0.328	0.583
$DRe(CO)_5$	16.37	16.98	0.281	0.330	0.582

[a] These force constants are *relatively* significant only to the first four (K_1, K_2) or three figures (K_c, $K_{c'}$, K_t). For the possible accuracy of these constants see the discussion in the text of the accompanying publication.[1b] [b] For definition of force constants, see Figure 3 of ref 1b. [c] With ν_{ReH} included. This calculation also yielded the following values: $K_{ReH} = 1.984$, $K_{H\text{-}CO}(cis) = 0.0006$, $K_{H\text{-}CO}(trans) = 0.225$ mdyne/A.

Several points should be noted. The mixing of ν_{ReH} with the carbonyl stretching modes provides a satisfactory explanation for the observed shift to lower energy of the axial carbonyl band upon deuteration. This is illustrated in Figure 3. In $HRe(CO)_5$, the A_1 purely carbonyl symmetry coordinate (mainly axial) and the A_1 purely ReH symmetry coordinate (vertical dotted lines, top row of figure) will mix and produce observed bands at higher and lower energies (vertical solid lines, second row of Figure 3).

In $DRe(CO)_5$, however, the A_1 purely carbonyl symmetry coordinate is separated by a large amount from A_1 ReD symmetry coordinate. Their mixing will be much decreased, and the observed bands (solid vertical lines, last row of figure) will suffer smaller energy shifts from the positions of the unmixed coordinates. Therefore, the carbonyl band assigned as A_1 (axial) is observed to shift to lower energy (diagonal arrow) when ν_{ReH} is replaced by ν_{ReD} in going from $HRe(CO)_5$ to $DRe(CO)_5$. The absence of similar effects in the spectra of the pentacarbonyl hydride and deuteride of manganese results no doubt from a smaller interaction in these derivatives between the ν_{CO} and ν_{MnH}. The shift, if any, on going to $DMn(CO)_5$ must be below the limits of error of observation of these bands.

The observed shift on deuteration only for the A_1 axial modes is reflected in the calculated interaction force constants between ν_{ReH} and ν_{CO}. The coupling of ν_{ReH} with *trans* ν_{CO} (about 0.22 mdyne/A) is about 400 times greater than the interaction between ν_{ReH} and *cis* ν_{CO} (0.0006 mdyne/A). This provides a quantitative measure of the *trans*-coupling effects of metal hydrides and carbonyl stretching modes observed in this work and also recently reported by Vaska for a number of other derivatives.[9]

The small changes in calculated force constants brought about by inclusion of ν_{ReH} in the calculations (fourth row, Table III) gives us some added confidence in the procedure of energy factoring. If the changes resulting from such a relatively close-lying vibration (at 1822 cm^{-1}) are small, it is expected that those which would result from the other nearest vibrations (metal-carbon stretching and metal-carbonyl bending) around 600 cm^{-1} would be even smaller still (assuming the coupling constants are of about the same order of magnitude) and can justifiably be left out when lack of data requires this. This makes it possible to carry out a vibrational analysis on an isolated portion of the spectrum such as the carbonyl stretching region.

Exchange Reaction. Confirmation of the ^{13}C assignments was accomplished by exchange with ^{13}C-enriched CO.

Both $HMn(CO)_5$ and $HRe(CO)_5$ exchange with ^{13}CO; the manganese compound exchanges at a much faster rate. The lower spectrum of Figure 1 shows $HRe(CO)_5$ after 24 hr exchange with 50% ^{13}C-enriched CO. Comparison with the normal spectrum of $HRe(CO)_5$ (upper spectrum) shows very definite changes. Peak b has grown almost equal in intensity to a, one of the fundamentals of the all-^{12}C molecule. The intensity of a has decreased as well since the total concentration of the all ^{12}C-molecule has been reduced. Comparison of spectra shows that g is much more intense in the labeled hydride and that peaks d and h have both increased. These changes confirm our assignment of these bands as ^{13}C-carbonyl modes and, since *all* the ^{13}CO peaks increase, indicate that both radial and axial carbonyls exchange. At no time in the exchange reaction does there appear to be a preference for radial or axial positions other than the increased probability of radial exchange since there are four radial to one axial carbonyls (assuming equal exchange rates for both groups). This is in agreement with Basolo, Braült, and Poë[15] who have found for $HMn(CO)_5$ from radiocarbon studies that all five CO's exchange at the same rate. The carbonyl spectrum after extensive exchange shows peaks characteristic of multiple ^{13}CO-substituted molecules.

Acknowledgment. We wish to thank Dr. J. M. Smith, Mr. D. Hendrickson, R. Bau, and R. Bagula for valuable discussions and for assistance at several times with the computer calculations. We also acknowledge the UCLA Computation Facility for making available intramurally supported computer time, and Miss Karen Mehner for preparation of the figures.

[15] F. Basolo, A. T. Braült, and A. J. Poë, *J. Chem. Soc.*, 676 (1964).

A Nuclear Magnetic Resonance Study of σ-Cyclopentadienyl(triethylphosphine)copper(I)[1]

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Received December 14, 1966

Abstract: The nmr spectrum of cyclopentadienyl(triethylphosphine)copper(I) has been examined as a function of temperature between 0 and −70°. The high-temperature spectrum of the cyclopentadienyl group consists of a single line; the corresponding low-temperature spectrum is composed of three lines having relative areas 2:2:1. The latter spectrum requires that the organometallic compound exist in solution as a copper σ-cyclopentadienide. Analysis of the spectral line shapes in the exchange-broadened region indicates that the averaging of chemical shifts observed at high temperatures must occur by either a sequence of 1,2 or 1,3 shifts of the metal atom around the cyclopentadienyl ring, and that it cannot take place by a sequence of random shifts. Chemical shift data are tentatively interpreted to support the 1,3-shift mechanism for the averaging.

Compounds containing a σ bond connecting carbon and copper(I) usually show a low order of thermal stability.[2] Details of the factors responsible for the thermal lability of this class of organometallic compounds are not well understood: the stability of the incipient radical formed during homolytic cleavage of the carbon–metal bond,[3] the ionic character of the bond,[4] and the magnitude of the energy separating the highest filled and lowest unfilled σ molecular orbitals[5] have been variously proposed to determine the stability of these and other transition metal alkyls.

As part of an investigation of the structural features influencing the rate of decomposition of several organocopper(I) reagents, we have had opportunity to examine some of the properties of cyclopentadienyl(triethylphosphine)copper(I).[6] Wilkinson and Piper have formulated this compound as a σ-cyclopentadienide, rather than a π-cyclopentadienide, on the basis of spectral evidence.[6] However, the thermal stability of this material is unexpectedly greater than that of other simple alkylcopper(I) compounds; moreover, its room-temperature nmr spectrum shows only a single sharp peak for the protons on the cyclopentadienyl ring.[6b] The possibility that cyclopentadienyl(triethylphosphine)copper is a member of the group of metal σ-cyclopentadienides characterized by rapid migration of the metal atom between carbon atoms in the cyclopentadienyl ring[6b–8] has led us to examine the temperature dependence of its nmr spectrum, in hope of learning more about its structure and the reasons for its unexpected thermal stability. In this paper we wish to report evidence which confirms the structure suggested by Piper and Wilkinson, and which sheds some light on the process which averages the chemical shifts of the cyclopentadienyl protons.

Results

The nmr spectrum of the cyclopentadienyl protons of cyclopentadienyl(triethylphosphine)copper in sulfur dioxide solution at 0° consists of a sharp line at 6.30 ppm downfield from internal tetramethylsilane (Figure 1); resonances due to triethylphosphine occur at higher field and are omitted from this figure. As the temperature of the sample is lowered, the cyclopentadienyl proton resonance broadens and splits into three lines

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[1] This research was supported by the National Science Foundation through Grant GP 2018. Calculations were carried out in part at the Massachusetts Institute of Technology Computation Center, Cambridge, Mass.

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