be present, but this is unlikely due to the solubility of this compound. On the basis of the analysis in Table I, 95% of the product has the approximate empirical formula $K_{11}Re_2Cl_{10}$. The mole reaction ratios of $K:K_2ReCl_6$ of about 5.6–5.8 indicate that the effective oxidation state of rhenium is below zero, having been reduced from +4 to −1 or −2. The great reducing equivalency of the solid product is also consistent with an oxidation state of rhenium below zero. Another explanation for the high reducing equivalency of the product would be the existence of hydridorhenate groups.

The brown solid product recovered from the reduction with potassium of ammonium hexabromorhenate(IV) is evidently a mixture of white potassium enneahydridorhenate(VII) and a rhenium–nitrogen compound.[10] Rhenium(IV) amide is possibly the source of nitrogen and the brown color, but, from the infrared spectrum, amide does not appear to be present. Rhenium(III) amide would be a possibility, also; Thompson found this compound to be formed by the reaction of potassium amide and rhenium(III) iodide in liquid ammonia.[11]

Potassium enneahydridorhenate(VII) and -technate(VII) have been produced in liquid ammonia by Ginsberg[12]; for the former, he added potassium to potassium perrhenate in ammonia which contained about 10% ethanol or water.

Acknowledgments.—We are indebted to Dr. A. P. Ginsberg for making available to us preprints of several of his papers and for supplying us with X-ray data and a powder diffraction photograph of K_2ReH_9. We thank Dr. W. H. Fletcher for helping with the interpretation of our infrared spectra. I. E. M. especially thanks the National Science Foundation for support under NSF-G15447.

[10] On the basis of our analytical results and the infrared spectrum, Dr. Ginsberg has suggested the product could be mainly a mixture of K_2ReH^9 and $(NH_4)_2ReH_9$.

[11] R. J. Thompson, Ph.D. Dissertation, Texas University, 1959.

[12] A. P. Ginsberg, private communication.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
NORTHERN ILLINOIS UNIVERSITY, DEKALB, ILLINOIS

Cyanide Stretching Frequencies of Some Mixed Ligand Complexes of Iron, Ruthenium, and Osmium

BY ALFRED A. SCHILT

Received February 24, 1964

The infrared absorption properties of some mixed cyanide and aromatic diimine complexes of iron, ruthenium, and osmium have been examined in an attempt to gain evidence concerning their configurations and bonding. This work was prompted in part by reports by Hamer and Orgel[1] and by Shriver[2] that the neutral dicyanobis(1,10-phenanthroline)iron(II) complex and its adducts with methyl sulfate, boron trifluoride, and diborane display two close-lying bands in the C≡N stretch region, suggesting a *cis* configuration for the complexes.[1,2] Since spectra obtained by the author in an earlier study[3] did not exhibit splitting of the cyanide frequencies, it was of interest to explore the possible effects of solvation and various recrystallization procedures on the spectra and also to extend the study to additional, related compounds.

Experimental

Analyzed samples of most of the complexes were available from earlier work: the osmium and ruthenium complexes,[3] the tetracyano complexes of iron(II) and (III),[4] and the dicyano complexes of iron(III).[4] Fresh samples of the dicyano complexes of iron(II) with 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) were prepared as described earlier but not recrystallized.[4] Assay of these by potentiometric titration with standard cerium(IV) sulfate in 6 *M* H_2SO_4 indicated equivalent weights corresponding to the formulas $[Fe(phen)_2(CN_2]\cdot 2H_2O$ and $[Fe(bipy)_2(CN)_2]\cdot 3H_2O$.

Spectra were obtained using a Beckman IR-8 spectrophotometer and the mull technique in Nujol. Frequency calibration was confirmed to within ±4 cm.$^{-1}$ by the spectrum of a polystyrene film.

Recrystallization from $CHCl_3$ involved dissolution in the boiling solvent, filtration, and evaporation of the filtrate to dryness to yield a chloroform solvated complex (as evidenced by strong absorption at 1350 cm.$^{-1}$). Heating above 100° gave the nonsolvated form. The formula $[Fe(phen)_2(CN)_2]\cdot 2CHCl_3$ was indicated by a loss in weight of 31.2% (theory, 33.8%) on drying the product at 120° for 1 hr. Recrystallization from concentrated H_2SO_4 by dilution with water was performed as previously described.[4] The solubility of $[Fe(bipy)_2(CN)_2]$ enabled recrystallization from hot water; the 1,10-phenanthroline analog was too insoluble for similar treatment. Water of solvation was removed by heating at 160° for 1 hr.

Results

Frequencies measured for the cyanide stretching motions are compiled in Table I. Relative intensities were estimated on the basis of peak heights, assigning the number 10 to the highest peak to be found for the compound and proportionately smaller numbers to the smaller peaks. Band widths at half-heights ranged from about 5 to 20 cm.$^{-1}$. As an illustration of typical band shape and resolution, spectra in the 2000 to 2400 cm.$^{-1}$ region for two of the complexes are shown in Fig. 1.

In the spectral region from 2000 to 625 cm.$^{-1}$ the 1,10-phenanthroline complexes showed little or no differences among themselves. The same was true for the bipyridine complexes. The only appreciable differences found were those expected due to the presence of water or chloroform of solvation. Since spectra in this region resemble those reported earlier for the simple *tris* aromatic diimine complexes of iron,[5] details are omitted here.

[1] N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

[2] D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963).

[3] A. A. Schilt, *ibid.*, **85**, 904 (1963).

[4] A. A. Schilt, *ibid.*, **82**, 3000 (1960).

[5] A. A. Schilt and R. C. Taylor, *J. Inorg. Nucl. Chem.*, **9**, 211 (1959).

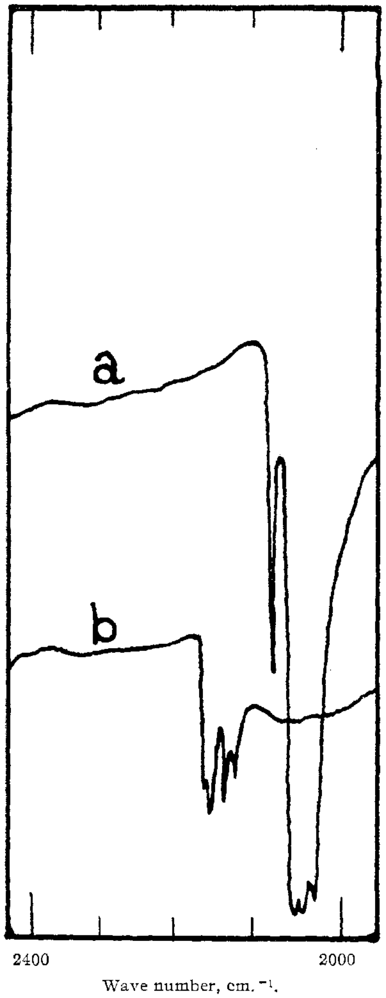

Fig. 1.—Absorption spectra of solids in Nujol: curve a, $K_2[Fe(bipy)(CN)_4]\cdot 3H_2O$; curve b, $H[Fe(bipy)(CN)_4]\cdot 2H_2O$.

Table I

Absorption Characteristics in the C≡N Stretch Region

Compound	Solvation	Recrystallized from	Absorption frequencies, cm.$^{-1}$ (and relative intensities)
$[Fe(phen)_2(CN)_2]$	$2H_2O$	...	2075 (8), 2062 (10)
	...	...	2075 (8), 2062 (10)
	$2CHCl_3$	$CHCl_3$	2066 (10) br
	...	$CHCl_3$	2075 (10)
	$2H_2O$	H_2SO_4	2075 (5), 2062 (10)
$[Fe(bipy)_2(CN)_2]$	$3H_2O$	...	2070 (8), 2066 (10), 2062 (10)
	...	...	2075 (8), 2062 (10)
	$3H_2O$	H_2O	2072 (10), 2068 (9)
	...	$CHCl_3$	2070 (10), 2062 (8)
	$3H_2O$	H_2SO_4	2068 (9), 2062 (10)
$[Ru(bipy)_2(CN)_2]$	$3H_2O$	H_2O	2041 (9) v br
	...	H_2O	2066 sh, 2060 (9)
	...	$CHCl_3$	2070 (9), 2053 (10)
$[Os(bipy)_2(CN)_2]$	$2H_2O$	H_2O	2050 sh, 2032 (8)
	...	H_2O	2060 sh, 2041 (10)
	...	$CHCl_3$	2066 (10), 2041 (10)
$K_2[Fe(phen)(CN)_4]$	$4H_2O$	H_2O	2080 (4), 2053 (10), 2040 (10)
$K_2[Fe(bipy)(CN)_4]$	$3H_2O$	H_2O	2080 (6), 2053 (10), 2040 (10), 2030 (9)
$[Fe(phen)_2(CN)_2]ClO_4$	...	...	2120 (0.5)
$[Fe(bipy)_2(CN)_2]ClO_4$	...	...	2120 (0.5)
$H[Fe(phen)(CN)_4]$	$2H_2O$	...	2150 (5), 2134 (4), 2119 (3)
$H[Fe(bipy)(CN)_4]$	$2H_2O$	...	2155 (4), 2150 (5) 2134 (4), 2119 (3)

Discussion

Although spectra obtained for solids can be misleading, a number of apparent consistencies in the results suggest that the splittings observed for the cyanide frequencies are due to coupling of stretching motions among the cyanide ligands rather than to solid state effects. Thus it can be predicted that coupling of cyanide stretching motions in the tetracyano complexes of this study, all of which are six-coordinate, could give rise to four close-lying frequencies. Two cyanide groups are *trans* to each other and all four are *cis* to another. Consistent with the C_{2v} symmetry of the complexes, there will be four nondegenerate CN stretching vibrations, each involving all four CN groups. Two will involve primarily *trans* cyanides and two primarily *cis* cyanides (one symmetric and one asymmetric for each). All four may be infrared active, although the symmetric *trans* vibration may be rather weak. Results appear to be consistent with prediction for $K_2[Fe(bipy)(CN)_4]$ and $H[Fe(bipy)(CN)_4]$. For the two analogous 1,10-phenanthroline compounds, the absence of a fourth band may be a result of either solid state effects altering the selection rules or inability of the instrument used to resolve the band. In the case of the dicyano complexes one could expect coupling to split the C≡N stretch frequency into symmetrical and antisymmetrical stretching motions. Both coupling motions would be infrared active in the *cis* complex, but only the antisymmetrical stretch would be active in the *trans* complex. Results obtained for $[Fe(phen)_2(CN)_2]$ crystallized from H_2O or H_2SO_4 therefore suggest that the *cis* configuration predominates. The spectrum of the same complex recovered from dissolution in hot $CHCl_3$ suggests that the *trans* form is produced almost exclusively.[5a]

Further rationalization, although more tenuous, can be advanced to support the suspicion that the *trans* form of the dicyano complexes would be favored by dissolution in $CHCl_3$. The premise is that formation of the nonpolar *trans* complex should be favored in a solvent of low acidity and dielectric strength such as $CHCl_3$, whereas, in more acidic solvents, the polar *cis* form should be favored by protonation[3,6] and dielectric effects.

There are a number of other interesting features shown by the data in Table I. The bands for the dicyanoiron(III) complexes appear at higher frequencies and are so weak that they are barely detectable. Any splitting is undetectable. Similar, but not such drastic changes in intensities are seen for the tetra-

---

(5a) Note Added in Proof.—Mössbauer spectra of $[Fe(phen)_2(CN)_2]$ before and after recrystallization from $CHCl_3$ show distinct differences, indicative of different ligand configurations. The author is grateful to Dr. Nils E. Erickson, University of Washington, for providing the spectra.

(6) A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 5779 (1960).

cyano complexes on oxidation to the iron(III) state. Other investigators have reported and discussed similar effects for iron cyanide complexes.[7-10] The bands for the solvated dicyano complexes differ from those of the nonsolvated, consistent with the fact that the cyanide ligands possess appreciable basic character.[2,3,6] On comparing the frequencies for [Fe(bipy)$_2$(CN)$_2$], [Ru(bipy)$_2$(CN)$_2$], and [Os(bipy)$_2$(CN)$_2$] recovered from CHCl$_3$, two regularities are evident: the splitting increases and both bands move to lower frequencies as the atomic number of the metal increases. The latter suggests increasing π-bond character between metal and cyanide ligands[1,10] going from iron to osmium. The relative basicities of the three complexes are also consistent with such a trend in bond character.[3]

(7) G. Emschwiller, *Compt. rend.*, **238**, 1414 (1954).

(8) E. F. G. Herington and W. Kynaston, *J. Chem. Soc.*, 3555 (1955).

(9) M. F. A. El-Sayed and R. K. Sheline, *J. Inorg. Nucl. Chem.*, **6**, 187 (1958).

(10) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF SOUTHERN CALIFORNIA,
LOS ANGELES, CALIFORNIA 90007

Enhancement of P-H Bonding in a Phosphine Monoborane

BY ANTON B. BURG

Received March 30, 1964

Infrared absorption bands for N-H stretching have quite generally been observed at lower frequencies when nitrogen is bonded to four atoms rather than three.[1] In phosphorus compounds, however, this rule seems to be reversed: four-coordinate phosphorus shows higher P-H stretching frequencies than are found for phosphines.[2] An explanation for this indication of stronger P-H bonding for four-coordinate P might be found in the rehybridization of phosphorus bonding orbitals when a fourth atom is attached.[3] For example, the phosphorus valence angles in the methylated phosphines all are below 100°,[4] meaning that the lone-pair electrons on P in a phosphine have far more s-character than such electrons on nitrogen; then a four-bonded phosphorus would offer a more nearly perfect tetrahedral 3sp^3 hybrid for the P-H bond than the s-deficient hybrid used for bonding H in a phosphine. This principle does not apply well to the corresponding nitrogen compounds, for the almost tetrahedral nitrogen hybrids in an amine would change little in forming the fourth bond.

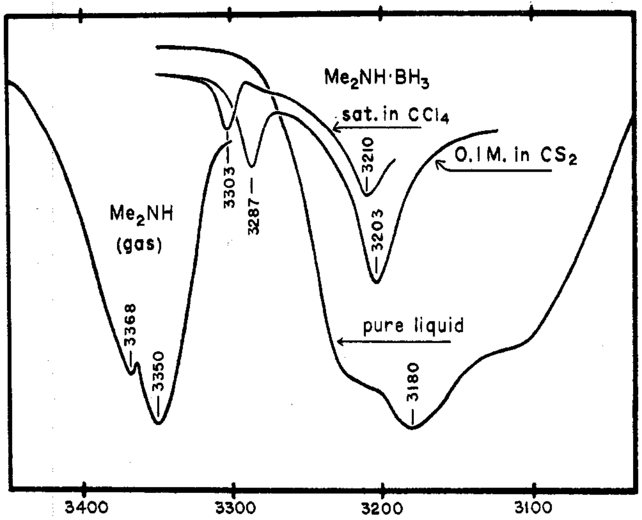

Fig. 1.—Comparison of the N-H stretching bands of $(CH_3)_2NH$ (gas) and $(CH_3)_2NH\cdot BH_3$ (liquid *vs.* solutions). Here and in Fig. 2 and 3 transmission is measured upward while the abscissa shows frequencies in cm.$^{-1}$.

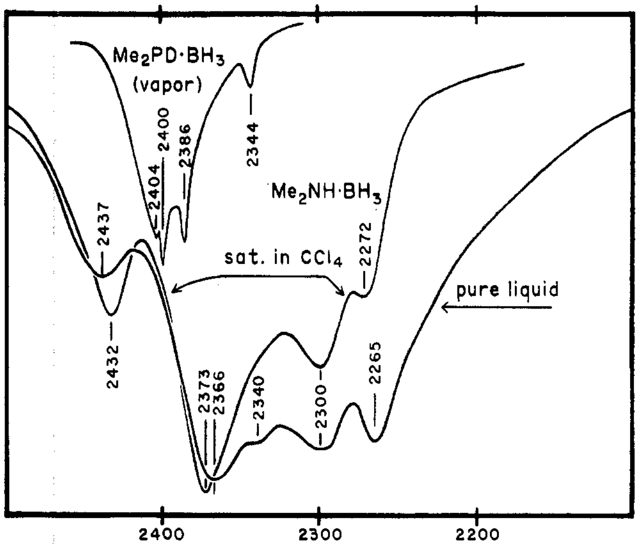

Fig. 2.—Comparison of the B-H stretching bands of $(CH_3)_2PD\cdot BH_3$ (vapor) and $(CH_3)_2NH\cdot BH_3$ (liquid and solution).

However, this P-H *vs.* N-H contrast has lacked a secure experimental basis, for the reported R$_3$N-H and R$_3$P-H spectra were for condensed phases, wherein N-H--X bonding effects could account for lower N-H frequencies; but for P-H compounds any such hydrogen-bonding effects would be far less important. Also, most of the reported four-bonded P compounds[2] had terminal P=O bonds, with uncertain effect upon the P-H bond energy.

A more effective comparison would be afforded by the BH$_3$ complexes of $(CH_3)_2NH$ and $(CH_3)_2PH$, for the acidic protons would not interact strongly with a bound BH$_3$ group, and any weak interaction would be minimized by dilution. In fact, the vapor-phase spectrum of $(CH_3)_2PH\cdot BH_3$ (or its D analogs, which avoid band superposition) does show a stronger P-H bond than is demonstrated for free gaseous $(CH_3)_2PH$;

---

(1) L. J. Bellamy, "Infra-red Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, New York, N. Y., 1958, pp. 203-262. The most obvious reason for lower N-H frequencies in undisturbed HNR$_3$ units would be the positive charge related to four-coordinate N, whereby the N-H bond would be weakened. Less important would be a slightly increased contribution by the four-bonded N to the reduced mass of the N-H oscillator.

(2) H. Schindlbauer and E. Steininger, *Monatsh.*, **92**, 868 (1961).

(3) J. H. Gibbs, *J. Chem. Phys.*, **22**, 1460 (1954).

(4) $(CH_3)_3P$: D. R. Lide, Jr., and D. E. Mann, *ibid.*, **29**, 914 (1958); $(CH_3)_2PH$: R. Nelson, *ibid.*, **39**, 2382 (1963); CH_3PH_2: T. Kojima, E. L. Breig, and C. C. Lin, *ibid.*, **35**, 2139 (1961).