was shown to have a K^+ to SiH_3^- ratio of 1.00:1.04. Other samples of potassium silyl prepared in this manner reacted with disilane, yielding silane as the only volatile product. The resulting solid yielded silane, disilane, and trisilane in varying amounts when treated with hydrogen chloride. However, most of the silicon remained in the solid after the reaction with hydrogen chloride.

The products but not their quantities can be accounted for by the reactions

$$Si_2H_6 \xrightarrow{KSiH_3} SiH_4 + (1/x)(SiH_2)_x \qquad (1)$$

$$KSiH_3 + Si_2H_6 \longrightarrow SiH_4 + KSi_2H_5 \qquad (2)$$

$$KSi_2H_5 + Si_2H_6 \longrightarrow SiH_4 + KSi_3H_7 \qquad (3)$$

$$KSi_2H_5 + HCl \longrightarrow Si_2H_6 + KCl \qquad (4)$$

$$KSi_3H_7 + HCl \longrightarrow Si_3H_8 + KCl \qquad (5)$$

Reaction 1 resembles the recently reported base-catalyzed condensations of silyl compounds.[2,3]

Experimental

General Experimental Methods.—The manipulative methods were those in general use for work under high vacuum. Disilane was prepared by the reduction of hexachlorodisilane with lithium aluminum hydride.[4] The volatile products were identified from vapor pressure measurements and by obtaining their infrared spectra and comparing these data with those reported in the literature.

Reaction between Potassium Hydride and Disilane.—Potassium hydride (0.78 mmole) and disilane (1.46 mmoles) were allowed to react in monoglyme for 24 hr. Silane (1.46 mmoles) was the only volatile product. Treatment of the solid products with excess hydrogen chloride yielded silane (0.45 mmole) and disilane (0.06 mmole).

Preparation of Potassium Silyl.—Disilane (0.48 mmole) was allowed to react with excess potassium hydride in monoglyme. After 24 hr., silane (0.46 mmole) was obtained and all of the disilane had been consumed. The solvent was distilled from the filtered solution and treatment of the resulting solid with excess hydrogen chloride yielded silane (0.200 mmole) and a trace of monoglyme. Analysis showed that 0.192 mg.-atom of potassium was present.

Before the solid was treated with hydrogen chloride, it was colored, but after the reaction it was white.

Reaction between Potassium Silyl and Disilane.—Potassium silyl (0.36 mmole, a quantity assumed from the amount of chloride ion found in the solid after the reaction with hydrogen chloride) was allowed to react with disilane (0.52 mmole) in monoglyme (4 ml.); after 24 hr., silane (0.49 mmole) was obtained and all of the disilane was consumed. Hydrogen chloride (0.59 mmole) was condensed onto the resulting solid after the solvent had been removed. The volatile materials were identified as silane (0.13 mmole), disilane (0.033 mmole), and trisilane (0.043 mmole).

Acknowledgments.—The authors are indebted to the U. S. Army Research Office (Durham) for financial support.

---

[2] R. Schaeffer and R. Wells, "Hydrogen Compounds of the Group IV Elements," F. G. A. Stone, Ed., Prentice-Hall, New York, N. Y., 1962, p. 28.

[3] A. G. MacDiarmid, *J. Inorg. Nucl. Chem.*, **25**, 1934 (1963).

[4] G. W. Bethke and M. K. Wilson, *J. Chem. Phys.*, **26**, 1107 (1957).

Correspondence

"Symbiotic" Ligands, Hard and Soft Central Atoms

Sir:

Pearson[1] recently published a fascinating paper entitled "Hard and Soft Acids and Bases." However, it is not certain that the central atoms in definite oxidation numbers can be arranged according to a single parameter, going from extreme Chatt–Ahrland (a) "hard acid" to (b) "soft acid." Thus, the (b) class seems to involve three rather disparate categories[2]: unusually low oxidation numbers; certain high oxidation numbers; and the s^2-family Sn(II), Sb(III), Tl(I), Pb(II), and Bi(III) showing (b) characteristics toward heavy halides and chalcogenides but definite (a) aversion against σ-bonded cyanides and amines. Many chemists would not admit that an element with highly varying oxidation number z, say manganese, would show (b) character as well for high z ($+4$ or $+7$) as for low z (-1 or $+1$), the maximum (a) tendencies occurring at an intermediate value of z, here $+2$. The M(a)–NCS and M(b)–SCN bonds formed by the ambidentate ligand thiocyanate are frequently used as a test case,[3] and it would not be surprising if Fe(II) was found to bind N and Fe(III) S, showing a maximum (a) tendency for $z = +2$. By the same token, the molybdenum(III) complex[4] $Mo(NCS)_6^{3-}$ is (a) and the dark red Mo(V) thiocyanates possibly belong to class (b). The question really is whether the covalent bonding becomes so much stronger for increasing z-values that the actual, fractional charge of the central atom rather decreases, promoting (b) behavior again. There is some evidence from the nephelauxetic effect[5] that this phenomenon occurs.

Closely connected with Pearson's ideas is the question why soft (b) ligands flock together in the same complexes, a true inorganic symbiosis. Bjerrum[6] emphasized that mixed complexes MX_aY_b of moderately different pairs of ligands, say water and ammonia, or fluoride and water, usually tend to be even more frequent than suggested by the statistical contribution to

---

[1] R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).

[2] C. K. Jørgensen, "Inorganic Complexes," Academic Press, London, 1963.

[3] A. Wojcicki and M. F. Farona, *Inorg. Chem.*, **3**, 151 (1964).

[4] J. Lewis, R. S. Nyholm, and P. W. Smith, *J. Chem. Soc.*, 4590 (1961).

[5] C. K. Jørgensen, *Progr. Inorg. Chem.*, **4**, 73 (1962).

[6] J. Bjerrum, *Chem. Rev.*, **46**, 381 (1950).

the higher entropy. Most exceptions can be explained away by high-spin–low-spin variations, making the intermediate complexes less favored, though, as Kida[7] pointed out, certain facts about cyanides are difficult to understand. The symbiosis is clear in cobalt(III) complexes, where $Co(NH_3)_5X^{2+}$ is far better bound for $X = F$ than I, showing (a) characteristics, whereas $Co(CN)_5X^{3-}$ is most stable with $X = I$ and not even known for $X = F$. The very soft base H^- also forms $Co(CN)_5H^{3-}$. We may remember Pauling's effect that, under equal circumstances, the characteristic coordination number of (b) ligands tends to be lower than of (a) ligands (*cf.* $CoCl_4^{2-}$ and $Co(H_2O)_6^{2+}$). This is not so much a question of larger atomic size as of an appropriate amount of electronic density being donated from a lower number of soft ligands.

The author and his colleague, Dr. H.-H. Schmidtke, attempt now to elucidate the symbiotic tendency by various MO calculations. Since the optical electronegativity[8] of the central atom nd shell increases monotonically with z, the empty $(n + 1)$s orbital may be more important. The nonmonotonic behavior as a function of z might be connected with the empty $(n + 1)$s orbital producing strong characteristics of a soft acid for low z, whereas the somewhat less pronounced (b) properties for very high z are caused by the near coincidence of the energies of a partly filled nd shell with the filled orbitals of the ligands. In the intermediate z range, covalent bonding is less conspicuous because both $(n + 1)$s and nd have much higher energy than the ligand orbitals.

(7) S. Kida, *Bull. Chem. Soc. Japan*, **34**, 962 (1961).
(8) C. K. Jørgensen, "Orbitals in Atoms and Molecules," Academic Press, London, 1962.

CYANAMID EUROPEAN RESEARCH INSTITUTE
COLOGNY (GENEVA), SWITZERLAND
C. KLIXBULL JØRGENSEN

RECEIVED MARCH 23, 1964

Importance of Steric Factors in the Type of Metal-Ligand Bonding, M-SCN or M-NCS, for Analogous Metal Complexes[1]

Sir:

It is well known that SCN^- forms both thiocyanato (M–SCN) and isothiocyanato (M–NCS) metal complexes, depending on the metal. Several authors[2] have pointed out that the change from M–NCS to M–SCN bonding coincides approximately, for different metals, to the change in halogenometal complex stabilities from $F^- > Cl^- > Br^- > I^-$ to $I^- > Br^- > Cl^- > F^-$. The first order is followed by class a and the second by class b metals.[3] Several explanations have been proposed for this difference, and it was most recently discussed by Pearson[4] in terms of the preference of a hard acid for a hard base and a soft acid for a soft base. Jørgensen[5] suggests that a given metal in either high or low oxidation state may exhibit M–SCN bonding, whereas in an intermediate oxidation state the bond type may be M–NCS.

Turco and Pecile[6] made the interesting and significant observation that for a given M, the type of bonding (M–SCN or M–NCS) depends on the nature of the other ligands in the complex (Table I). That complexes of Pd(II) and Pt(II) containing NH_3 are of the type M–SCN, compared with analogous $P(C_2H_5)_3$ systems being M–NCS, was explained on the basis of the π-bonding of the phosphine. Wojcicki and Farona[7] have recently prepared several substituted manganese carbonyl compounds containing Mn–SCN and Mn–NCS. It was suggested that the basicity of the ligands in these systems may play an important role in determining the nature of SCN^- bonding. Further study[8] indicates that steric factors may also be important.

Table I

Effect of Ligands on the Type of Bonding, M–SCN or M–NCS, for Analogous Metal Complexes

No.	M–SCN complexes	Ref.	No.	M–NCS complexes	Ref.
1	$Pt(NH_3)_2(SCN)_2$	*a*	**2**	$Pt(P(C_2H_5)_3)_2(NCS)_2$	*a*
3	$Pd(NH_3)_2(SCN)_2$	*a*	**4**	$Pd(P(C_2H_5)_3)_2(NCS)_2$	*a*
5	$Pd(Sb(C_6H_5)_3)_2(SCN)_2$	*b*	**6**	$Pd(P(C_6H_5)_3)_2(NCS)_2$	*b*
7	$Pd(\gamma\text{-pic})_2(SCN)_2$	*b*	**8**	$Pd(py)_2(NCS)_2$	*b*
9	$[Pd(dien)SCN]^+$	*c*	**10**	$[Pd((C_2H_5)_4dien)NCS]^+$	*c*

[a] Reference 6. [b] J. L. Burmeister, doctorate thesis, Northwestern University, Evanston, Ill., 1964. γ-pic = γ-picoline; py = pyridine. [c] W. H. Baddley, doctorate thesis, Northwestern University, Evanston, Ill., 1964. dien = $NH_2C_2H_4NHC_2H_4NH_2$; $(C_2H_5)_4$dien = $(C_2H_5)_2NC_2H_4NHC_2H_4N(C_2H_5)_2$.

The importance of steric factors on the nature of SCN^- linkage in metal complexes has not previously been discussed in the literature. Hence, we wish to report the synthesis of the complex $[Pd((C_2H_5)_4dien)NCS]^+$ in which the Pd–NCS bonding is believed to be determined by steric factors. The compound $[Pd((C_2H_5)_4dien)NCS]SCN$ was prepared by treating an aqueous solution of $[Pd((C_2H_5)_4dien)Cl]Cl$[9] with excess KSCN at room temperature. Cooling the solution in an ice bath caused a light yellow solid to separate. This substance was recrystallized from warm aqueous ethanol. *Anal.* Calcd. for $PdC_{14}H_{29}N_5S_2$: C, 38.39; H, 6.67. Found: C, 38.59; H, 6.63. The conductivity of a 0.001 *M* solution in water is 91 ohm^{-1} mole^{-1}. The ultraviolet absorption spectrum shows a maximum at 325 mμ with ϵ = 1360 l. mole^{-1} cm.$^{-1}$. The infrared spectrum is consistent with an M–NCS linkage due to absorptions at 832 and 2100 cm.$^{-1}$ in a Nujol mull, corresponding to the C–S and C–N stretch-

---

(1) Presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.
(2) I. Lindquist and B. Strandberg, *Acta Cryst.*, **10**, 176 (1957); P. C. H. Mitchell and R. J. P. Williams, *J. Chem. Soc.*, 1912 (1960).
(3) S. Ahrland, J. Chatt, and N. R. Davies, *Quart. Rev.* (London), **12**, 265 (1958).
(4) R. G. Pearson, *J. Am. Chem. Soc.*, **85**, 3533 (1963).
(5) C. K. Jørgensen *Inorg. Chem.*, **3**, 1201 (1964).
(6) A. Turco and C. Pecile, *Nature*, **191**, 66 (1961).
(7) A. Wojcicki and M. F. Farona, *Inorg. Chem.*, **3**, 151 (1964).
(8) A. Wojcicki and M. F. Farona, Paper presented at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.
(9) W. H. Baddley and F. Basolo, *J. Am. Chem. Soc.*, **86**, 2075 (1964).