much faster than are the reactions of $Mn_2(CO)_{10}$ and other $Mn_2(CO)_9L$ and $Mn_2(CO)_8L_2$ derivatives.[6] This way the reaction can be stopped before $MnNO(CO)_4$ reacts further with NO or L. The starting material $Mn_2(CO)_8[P(C_6H_5)_3]_2$ can be prepared photochemically by the method of Osborne and Stiddard[7] or very conveniently by the thermal reaction described here.

$Mn(NO)_3CO$.—Barraclough and Lewis[8] prepared this compound in low yield by the reaction of gaseous NO with solid $Mn(CO)_5I$ or $Mn_2(CO)_8I_2$.

As mentioned above, it was observed that $MnNO(CO)_4$ produced in (1) reacts further with NO. This was followed up and it was found that under appropriate conditions the primary product is $Mn(NO)_3CO$. Thus, a new and convenient preparation of this compound is represented by

$$MnNO(CO)_4 + 2NO \longrightarrow Mn(NO)_3CO + 3CO \qquad (5)$$

The reaction is carried out at 90° in high-boiling solvents, from which $Mn(NO)_3CO$ can be separated by distillation under vacuum. The reaction time depends on the amount of starting material used. Starting with 160 mg of $MnNO(CO)_4$ we obtained $Mn(NO)_3CO$ within 4 min in 50% yield. Generally the reaction with NO has to be carried out until all of the $MnNO(CO)_4$ is consumed, since the two manganese compounds are difficult to separate. However, the reaction should be stopped as soon as possible, since $Mn(NO)_3CO$ decomposes in the presence of excess NO. Fortunately, the infrared spectra of the two compounds differ, making it convenient to determine the extent of reaction.

Experimental Section

All of the reactions and experimental operations were carried out under nitrogen with careful exclusion of oxygen and using anhydrous solvents. The usual techniques involving Schlenk tubes and Frittes were employed. Manipulations requiring little time were done in the room light, but, for longer periods of time, light was excluded from flasks containing $MnNO(CO)_4$ and $Mn(NO)_3CO$. The NO was purified by successively passing it through a concentrated aqueous solution of NaOH, H_2SO_4, KOH, and P_4O_{10}. The $Mn_2(CO)_{10}$ was purchased from Alpha Inorganics.

$Mn_2(CO)_8[P(C_6H_5)_3]_2$.—In a 250-ml flask, equipped with reflux condenser and mercury bubbler, 3 g of freshly sublimed $Mn_2(CO)_{10}$ and 9 g of $P(C_6H_5)_3$ in 150 ml of *p*-xylene were heated for about 15 hr at 120°. The reaction mixture, which contains $Mn_2(CO)_8[P(C_6H_5)_3]_2$, $Mn_2(CO)_9P(C_6H_5)_3$, and a little unreacted $Mn_2(CO)_{10}$, was cooled to room temperature and allowed to stand for several hours. During this time crystals of $Mn_2(CO)_8[P(C_6H_5)_3]_2$ separated from solution and were collected on a filter (4.2 g). The mother liquor was concentrated to *ca.* 50 ml and allowed to stand at room temperature in the room light for 3 days. During this time an additional 2 g of product separated from solution. The product, obtained in 95% yield, in *p*-xylene solution has an infrared spectrum in the C–O stretching region with bands at 1980 w and 1959 s cm^{-1} in agreement with the published[7] values for $Mn_2(CO)_8[P(C_6H_5)_3]_2$.

$MnNO(CO)_4$.—A suspension of finely ground $Mn_2(CO)_8[P(C_6H_5)_3]_2$ in 150 ml of tetraline was heated for 3 min to 95° under continuous shaking. After the compound was completely dissolved and NO was bubbled through the hot solution for 50 sec, the NO gas was turned off. A gentle stream of N_2 was passed through the solution which was also immediately cooled to room temperature using an ice bath. The reaction flask was then connected to a cold trap (−78°) using normal thick-wall Tygon tubing. The system was evacuated and allowed to distil overnight (or faster under vigorous stirring of the tetraline solution). The product was purified by several redistillations which did not take more than 2–3 min each (during the first redistillation from a mixture with some tetraline the flask should be shaken). A yield of 160–180 mg (75–83%) of $MnNO(CO)_4$ was obtained which can be kept in a Schlenk tube under nitrogen and in the dark. A *p*-xylene solution of the compound has an infrared spectrum with absorption bands at 2106 w, 2034 s, 1979 s, and 1763 s cm in agreement with the published values.[4]

Whenever tetraline in this preparation was replaced with *p*-xylene as the solvent, it distilled along with $MnNO(CO)_4$. A solution of *ca.* 50 ml was obtained which could be used directly for the preparation of $Mn(NO)_3CO$ and for other purposes.

$Mn(NO)_3CO$.—A solution of 160 mg of $MnNO(CO)_4$ in 40 ml of *p*-xylene was heated to 90° for 3 min. Gaseous NO was then passed through the hot solution for 4 min at which time the NO was turned off. This was replaced by a gentle stream of N_2 and the solution was immediately cooled to room temperature by means of an ice bath. The reaction mixture was passed through a fine filter and the product was distilled into a cold trap as described above. A yield of 70 mg (50%) of $Mn(NO)_3CO$ in *p*-xylene solution was obtained (determined by means of infrared measurements). The compound has an infrared spectrum with bands at 2095 m, 1824 m, and 1731 s in agreement with the published values.[8] The compound can be kept frozen in the dark and under nitrogen.

If the amount of starting materials ($Mn_2(CO)_8[P(C_6H_5)_3]_2$ or $MnNO(CO)_4$) is changed in the preceding preparations, the reaction times with NO also have to be changed in order to obtain the best yields. Whenever the reaction mixture starting with $Mn_2(CO)_8[P(C_6H_5)_3]_2$ turns green, this indicates that $Mn(NO)_3L$ ($L = CO, P(C_6H_5)_3$) has been formed. The reactions can be followed by taking infrared spectra of small samples from the reaction solutions in the CO or NO stretching region.

Acknowledgment.—This research is supported by National Science Foundation Grant GP-2505 to Northwestern University and the Technischen Hochschule, Munich. We wish to thank Professor E. O. Fischer for helpful suggestions and interest in this research.

---

[7] A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 634 (1964).

[8] C. G. Barraclough and J. Lewis, *ibid.*, 4842 (1960).

Correspondence

Use of the Edwards Equation to Determine Hardness of Acids

Sir:

The utility of the concept of soft and hard acids and bases[1] was recently emphasized by an international symposium held on this subject.[2] One limitation to the application of this concept would appear to be the difficulty of unambiguously classifying acids and bases as hard or soft. In the case of bases, a numerical order-

---

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

[2] Condensation of the symposium papers appeared in *Chem. Eng. News*, **43** 90 (May 31, 1965).

ing is possible based on the logarithm of the rate constant for the reaction of various nucleophiles with *trans*-dichlorodipyridineplatinum(II).[3] It is also possible to get an ordering of softness[4] from the C_B/E_B ratios of the Drago–Wayland equation,[5] where C_B and E_B are constants assigned to Lewis bases in a fashion designed to make C_B reflect the covalent contribution and E_B reflect the electrostatic contribution of the base to the enthalpy of formation of a molecular addition compound. Neither of these approaches is applicable to the determination of the hardness of metal ions. We wish to report here the use of α/β ratios of the Edwards equation[6] as a measure of the hardness of metal ions. Recent stability constant data,[7] β_n, were used along with what we felt to be the best assignments[8] of H (ligand $pK_a + 1.74$) and E_n (the ligand nucleophilicity parameter) to obtain α and β values of the Edwards equation. A computer program was used to fit a rearranged form of the Edwards equation

$$\log [\beta_n + 1.74n]/H = \alpha E_n/H + \beta$$

Although this method of fitting the Edwards equation has been questioned by Edwards,[9] its simplicity has led us and others[10] to use it. Our results are shown in Table I along with the Pearson classification. Hard acids in general have a low α (sensitivity to nucleophilic ligand character, or polarizability) and a high β (sensitivity to basicity of ligand toward protons). The α/β ratio allows simultaneous consideration of both factors and should be of value in assigning hardness to more metal ions as further stability constant data become available. Negative α or β values are interpretable as due to an overlap of the factors making up H and E_n.[8] Since these negative α or β values will always be small, the absolute value of α/β will unambiguously put metals with negative α values in the hard classification and metals with negative β values in the soft classification.

TABLE I

A COMPARISON OF α/β WITH HARDNESS

Metal ion	α	β	α/β^a	Hardness[b]
Hg^{2+}	5.786	−0.031	187	S
Cu^+	4.060	0.143	28.4	S
Ag^+	2.812	0.171	16.5	S
Pb^{2+}	1.771	0.110	16.1	B
Sr^{2+}	1.382	0.094	13.0	H
Cd^{2+}	2.132	0.171	12.5	S
Cu^{2+}	2.259	0.233	9.7	B
Mn^{2+}	1.438	0.166	8.7	H
In^{3+}	2.442	0.353	6.9	H
Mg^{2+}	1.402	0.243	5.8	H
Zn^{2+}	1.367	0.252	5.4	B
Ga^{3+}	3.795	0.767	5.0	H
Ba^{2+}	1.786	0.411	4.4	H
Fe^{3+}	1.939	0.523	3.7	H
Ca^{2+}	1.073	0.327	3.5	H
Al^{3+}	−0.749	1.339	0.6	H
H^+	0.000	1.000	0.0	H

[a] Ratio from monoligated complex; sign neglected. [b] Pearson classification;[3] S = soft, H = hard, B = borderline. [c] Not classified by Pearson; predicted from α/β ratio.

Acknowledgment.—We wish to thank The Ethyl Corp. for a fellowship supporting A. Y. for the academic year 1964–1965, Myron J. DeLong for assistance in the computer work, and the National Science Foundation for a grant to the University of Cincinnati Computing Center (Grant No. 19281).

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CINCINNATI
CINCINNATI, OHIO 45221
AUSTIN YINGST
DARL H. MCDANIEL

RECEIVED JULY 29, 1966

---

[3] R. G. Pearson, *Science*, **151**, 172 (1966).

[4] See ref 3, particularly footnote 29.

[5] R. S. Drago and B. B. Wayland, *J. Am. Chem. Soc.*, **87**, 3571 (1965).

[6] J. O. Edwards, *ibid.*, **76**, 1541 (1954).

[7] L. G. Sillén and A. E. Martell, "Stability Constants of Metal Ion Complexes," The Chemical Society, London, 1954.

[8] Sources the same as those cited for calculations in D. H. McDaniel and A. Yingst, *J. Am. Chem. Soc.*, **86**, 1334 (1964).

[9] J. O. Edwards, *ibid.*, **78**, 1819 (1956).

[10] R. E. Davis, R. Nehring, S. P. Molnar, and L. A. Suba, *Tetrahedron Letters*, 885 (1966).

A Correlation between the Boron–Hydrogen Stretching Frequency and the Boron–Hydrogen Nuclear Magnetic Coupling Constant

Sir:

It is well accepted that the ^{13}C–H spin coupling constants, J_{CH}, are mainly determined by the s character of the carbon orbital.[1] On the other hand, the CH stretching force constants have also been recognized to depend upon the hybridization of the carbon orbital.[2,3] These two facts suggest a simple correlation between the two variables, and, in practice, Brown and Puckett[4] have examined methyl groups attached to various atoms or groups to find a linear correlation. We have independently noticed a similar correlation between the two variables to hold for various types of B–H bond.[5] The infrared and nmr data obtained from literature sources are collected in Table I and shown graphically in Figure 1. Here, the stretching frequency, ν_{BH}, was used instead of the force constant which necessitates troublesome calculations to obtain, because the B–H stretching vibrations are highly localized within the B–H bonds. For molecules having more than one B–H bond are cited the weighted average values of the symmetric and asymmetric stretching frequencies calculated by the average rule.[6] The linearity of the plot is quite satisfactory except for the point of aluminum borohydride which will be referred to later. In contrast to the B–H bond, the inclusion of C–H bonds other than the methyl group, *e.g.*, aldehydes,

---

[1] C. Juan and H. S. Gutowsky, *J. Chem. Phys.*, **37**, 2198 (1962).

[2] A. D. Walsh, *Discussions Faraday Soc.*, **2**, 18 (1947).

[3] C. A. Coulson, "Valence," Oxford University Press, New York, N. Y., 1952, p 200; L. J. Bellamy, "The Infrared Spectra of Complex Molecules," Methuen and Co., Ltd., London, 1958.

[4] T. L. Brown and J. C. Puckett, *J. Chem. Phys.*, **44**, 2238 (1966).

[5] This paper was presented at the 19th Annual Meeting of Chemical Society of Japan, Tokyo, April 3, 1966, Preprint part I, IC305.

[6] W. J. Lehmann, *J. Mol. Spectry.*, **7**, 261 (1961).