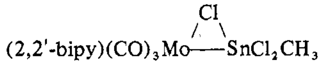
contains $SnCl_3^-$. A donor-adduct complex of $SnCl_4$, ((1,5-cyclooctadiene)RhCl)$_2$·2$SnCl_4$, has been prepared and found to have a strong ν(Sn–Cl) band at 313 cm^{-1} (Nujol mull).[16]

There is precedence for the reaction between I and Cl^-, eq 6, if it is assumed that the donor-adduct isomer is the reactive form.[5,16,17] Although an oxidative addition isomer is not expected to react with Cl^-, it will participate in the net reaction if it is in rapid equilibrium with a reactive, donor-adduct isomer. The evidence for a rapid interconversion between isomers had been given above. It should also be noted that if less than stoichiometric amounts of Cl^- are added to solutions of I in dichloromethane, ν(CO) for *trans*-IrCl(CO)-$(PPh_3)_2$ appears and the intensities of *both* ν(CO) bands for I decrease.

The structural details of the donor-adduct isomer may resemble the simple metal–metal interaction found in (h^5-C_5H_5)$(CO)_2$Co·$HgCl_2$[18] or the halide-bridged structure found, for example, in[19]



$$(2,2'\text{-bipy})(CO)_3Mo\overset{Cl}{\frown}SnCl_2CH_3$$

Unfortunately, we have been unable to grow suitable crystals for an X-ray diffraction study.

Discussion of the Isomerism. Kinetic[20,21] and synthetic[5,22,23] evidence is available which indicates that reactions between metal complexes and HgX_2 or SnX_4 may proceed in a stepwise fashion, with the first step involving donor-adduct formation and the second, oxidation, *e.g.*, eq 8.[24] In

$$(h^5\text{-}C_5H_5)Rh(CO)_2 + SnCl_4 \rightarrow (h^5\text{-}C_5H_5)(CO)_2Rh(SnCl_4) \rightarrow (h^5\text{-}C_5H_5)(CO)ClRh(SnCl_3) + CO \qquad (8)$$

most reactions, either the donor-adduct or the oxidized form is favored energetically, and a single product is obtained. In net oxidation reactions, it appears that either step can be rate limiting.[20,21,25]

The case reported here is unusual in that donor–adduct and oxidative addition isomers appear to be in measurable equilibrium both in solution and in the solid state. The energetics relating the two isomers are clearly closely balanced, as evidenced by the solvent dependence of the equilibrium. A closely related isomerism may exist in complexes like (bipy)$(CO)_3$Mo($SnCl_4$), where the likely isomers are chloride bridged, previously shown, and nonbridged (bipy)-$(CO)_3$ClMo($SnCl_3$) oxidative elimination products.[19,25]

The existence of rapidly equilibrating intramolecular redox isomers in $(PPh_3)_2$(CO)ClIr($SnCl_4$) may have important implications for the formulation of the products of reactions between metal complexes and HgX_2 and SnX_4 and for an understanding of the factors important in the microscopic reverse of oxidative addition, reductive elimination.

Registry No. *trans*-IrCl(CO)$(PPh_3)_2$, 15318-31-7; $(PPh_3)_2$-(CO)ClIr($SnCl_4$), 40813-53-4; $(PPh_3)_2$(CO)ClIr($SnCl_4$), 39310-35-5; $(PPh_3)_2$(CO)ClIr(CH_3SnCl_3), 39310-36-6; IrCl($SnCl_3$)-(CO)(PPh_3), 40903-18-2; $(PPh_3)_2$(CO)Cl_2Ir(HgCl), 14515-76-

Acknowledgments. Acknowledgments are made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, and to the Materials Research Center, University of North Carolina, under Grant GH 33632 for support of this research.

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Preparation and Properties of Nonaborane(13) Carbonyl[1]

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In the thermal decomposition of borane carbonyls such as BH_3CO and B_4H_8CO, carbon monoxide and the parent borane fragments are formed initially.[2-7] Carbon monoxide is a weak nucleophile and has little effect on subsequent reactions. This fact makes borane carbonyls useful precursors to study the chemistry of reactive borane fragments such as ligand exchange reactions, hydrogenation, and hydroboration.[8-13] In addition, they may be precursors of some less stable boranes.

As a promising source of a B_9H_{13} fragment we wish to report the preparation of $B_9H_{13}CO$. This compound is formed when *i*-B_9H_{15} is decomposed at −30° in pentane solution under 25 atm of CO. In a typical reaction *i*-B_9H_{15} was prepared by refluxing 2.26 g of KB_9H_{14} with liquid hydrogen chloride in a 200-ml heavy-walled flask equipped with a break-off tip.[14,15] Unreacted hydrogen chloride was distilled from the flask at −78° and the last traces were pumped off under high vacuum. Dried *n*-pentane, 100 ml, and about a tenfold excess of CO were condensed into the reaction flask at −196°. The amount of CO was controlled such that 30 atm of pressure would not be exceeded if the sample was accidently warmed to room temperature. The

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(1) Studies of Boranes. XXXVI. For paper XXXV of this series, see R. R. Rietz and R. Schaeffer, *J. Amer. Chem. Soc.*, **95**, 4580 (1973).

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Table I. Partial Mass Spectrum of $B_9H_{13}{\cdot}CO$ at 70 eV ($^{11}B_9H_{13}{\cdot}CO$ = 140 mass units)

m/e	I/I_0	*m/e*	I/I_0
65	2.0	95	4.4
66	6.6	96	8.8
67	6.6	97	16.6
68	7.6	98	20.0
69	6.6	99	24.4
70	3.0	100	31.1
71	3.0	101	31.1
72	2.0	102	37.7
73	<1.0	103	68.8
74	<1.0	104	100.0
75	2.0	105	97.8
76	6.1	106	53.3
77	8.8	107	33.3
78	11.1	108	42.3
79	11.1	109	39.9
80	6.0	110	19.8
81	4.4	111	1.0
82	2.0	112	1.0
83	2.0	113-138	<1.0
84	1.0	129	2.2
85	4.4	130	9.4
86	13.2	131	24.3
87	19.8	132	42.5
88	19.8	133	42.3
89	24.4	134	22.2
90	30.0	135	13.2
91	28.8	136	19.8
92	23.3	137	19.8
93	19.8	138	11.1
94	9.5	139	1.6
		140	1.0

flask was sealed and the frozen contents were slowly thawed; the milky slurry was stirred for 6 hr at −30°. The reaction flask was then sealed to a multiple low-temperature filtration apparatus and opened, and excess CO was pumped away at −196°. Filtration at −20° gave a water-clear pentane solution from which $B_9H_{13}CO$ was precipitated in fine needle-like crystals by slowly cooling the solution to −60° and $B_9H_{13}CO$ (1.58 g, mp 40.8°) was recovered by filtration (yield 75% on KB_9H_{14}). Elemental analysis (experimental values) in per cent: C, 8.67 (8.63); H, 9.46 (9.41); B, 70.31 (70.40).

The compound is somewhat air-sensitive but stable at room temperature in sealed tubes and sublimes undecomposed under high vacuum. The greater stability of $B_9H_{13}CO$ than observed in the cases of carbonyls containing one to four boron atoms was foreshadowed by the prior observation of Knoth, *et al.*, on the high stability of large-cage polyborane carbonyls such as $B_{12}H_{10}(CO)_2$.[16]

The mass spectrum at 70 eV using a cold gas inlet system showed two major groups of peaks extending to *m/e* 140 and 112 (Table I). Both groups of peaks have a similar intensity pattern with a difference of 28 mass units.[17] An exact mass match for the cutoff peak is 140.1811 (corresponding to the $^{11}B_9H_{13}CO^+$ ion 140.1804).

The infrared absorption bands of the solid compound (in cm^{-1}) are 2565 (vvs), 2160 (vvs), 2000 (vvw, sh), 1880 (vvw), 1650 (vvw), 1480 (vw), 1350 (vw), 1040 (w), 1005 (vw), 970 (vw, sh), 945 (w), 905 (vw), 838 (vw), and 785 (vw). The dominant bands are the valence modes B-H (2565 cm^{-1}) and BC-O (2160 cm^{-1}).

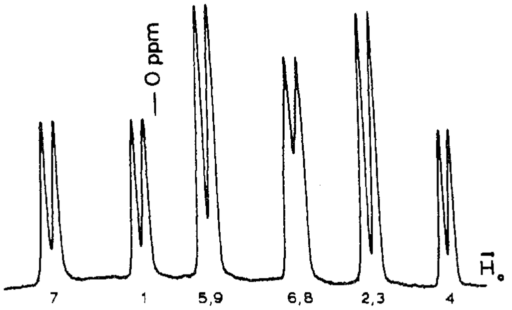

Figure 1. The 70.6-MHz ^{11}B nmr spectrum of $B_9H_{13}CO$ in *n*-pentane. Chemical shifts (in ppm relative to BF_3 etherate) and coupling constants (in cps): (7) −20.3, 155; (1) −3.6, 145; (5,9) +8.8, 150; (6,8) +25.3, 155, fine str ~50; (2,3) +38.9, 155; (4) +52.8, 130.

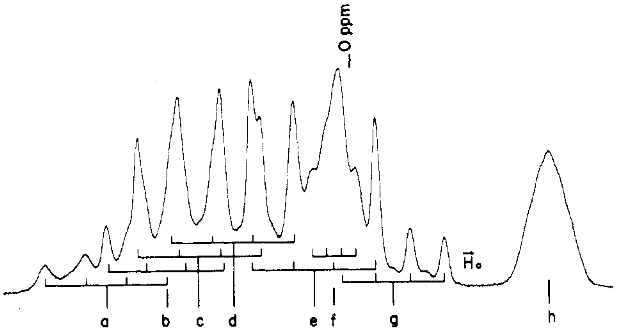

Figure 2. The 220-MHz ^1H nmr spectrum of $B_9H_{13}CO$ in $DCCl_3$. Chemical shifts (in ppm, external TMS) and coupling constants (in cps): (a) −4.05, 150; (b) −3.18, 145; (c) −2.45, 155; (d) −2.09, 150; (e) −0.57, 151; (f) −0.23, 55; (g) −0.042, 130; (h) +3.25.

The 70.6-MHz ^{11}B nmr spectrum shows a 1:1:2:2:2:1 pattern with six nonequivalent boron environments and is consistent with the C_s symmetry of the $B_9H_{13}NCCH_3$ molecule.[18] The six doublets can be readily assigned by comparison with the ^{11}B nmr spectra of specifically substituted B_9H_{13}-ligand compounds.[19] (See Figure 1.) Each band of the 6,8 doublet shows poorly resolved fine structure with a coupling constant of about 40-50 Hz.

In the 220-MHz ^1H nmr spectrum a complex pattern of overlapping quartets and one broad singlet of area ratio 11.2:2 is observed. This indicates that there are only two bridging protons in the molecule. With BH_2 groups in the 6 and 8 positions of the 11 nonbridging protons, there should be four quartets of area two and three quartets of area one. The three quartets a, b, and g of area one are found together with three quartets of area two, c, d, and e (Figure 2). Their coupling constants correspond to those observed in the ^{11}B nmr spectrum. We think that the fourth quartet, f, of area two, with the unusual small coupling constant, $J_{^{11}B-^1H}$ = 55 Hz, is due to "unique" protons that may occupy the axial positions in the BH_2 groups on the boron atoms 6 and 8. Together with the equatorial protons they could form BH_2 groups comparable to the unusual BH_2 group in the 1 position of B_5H_{11}, where a coupling constant of $J_{^{11}B-H_{\mu}^{*}}$ = 51 Hz is found.[20,21] Obviously, the axial-equatorial assignment is at best an "informed" guess.

Precession photographs establish that the crystal has an orthorhombic unit cell: a = 8.31 Å; b = 9.95 Å; and c =

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11.11 Å. With the stronger Lewis base dimethyl sulfide, $B_9H_{13}CO$ can be converted into $B_9H_{13}SMe_2$ at temperatures above 40° with loss of CO as ligand. The reactions of $B_9H_{13}CO$ with amines are more complex and CO seems to be retained probably forming carbonic acid derivatives.[10,22]

(22) A. B. Burg and H. I. Schlesinger, *J. Amer. Chem. Soc.*, 59, 780 (1937).

Registry No. $B_9H_{13}CO$, 40583-41-3; *i*-B_9H_{15}, 12447-79-9; KB_9H_{14}, 39296-28-1; $B_9H_{13}SMe_2$, 32357-02-1; CO, 630-08-0; dimethyl sulfide, 75-18-3.

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Correspondence

On Pearson's Quantitative Statement of HSAB

Sir:

A recent report[1] of a quantitative test of the HSAB concept was followed by an article taking exception to the test.[2] The issues raised have clouded the picture, made our criticisms appear semantic, and prompted this response. The hard–soft model has its basis in arguments which are related to the strength of bonding. It is then applied and offered as an explanation for observations on systems in which kinetic control, entropy of adduct formation, solvation effects (enthalpic and entropic), ion-pairing effects (enthalpic and entropic), or lattice energy effects (enthalpic and entropic) are large and could even dominate the observation. When HSAB considerations are employed on these systems, one is implying that the soft–soft or hard–hard interactions, which supposedly influence the bonding, dominate the chemistry. The *E* and *C* approach should not be viewed as an alternative to this kind of science. The *E* and *C* model does predict the strength of interaction quantitatively on systems in which the data employed are related to the strength of binding. If the HSAB ideas are correct models for the strength of bonding, it must be capable of being expressed in a mathematical form and do well on data related to the strength of interaction. If it does not, it should be discarded and replaced by a more correct interpretation of the strength of binding. This was the object of our previous note.

Knowledge of the factors influencing the strength of interaction is important in correlating trends in reactivity and in suggesting new syntheses or experiments. This has been amply demonstrated by the wide acceptance and utilization of the HSAB ideas. The more correct model should be even more powerful in this kind of application.

Pearson took issue with our quantitative statement of the rule that "hard acids prefer to bind to hard bases and soft acids prefer to bind to soft bases" with the equation[2a]

$$-\Delta H = H_A H_B + (K - H_A)(K' - H_B) \tag{1}$$

This rather obvious mathematical translation of the above rule was criticized because we failed to incorporate intrinsic strength. As mentioned in the note added in proof,[1] in a vast majority of the qualitative applications of HSAB, strength is not considered, so, apparently, the authors believe that just hard and soft work well most of the time. We felt that if the concept was correct and was being correctly applied (most of the time), eq 1 should work well most of the time on data related to the strength of bonding. It did not. Next, we shall examine whether or not the situation can be rectified with intrinsic strength as has been suggested.[2]

We shall refer to the addition of strength as the HSSAB (hardness, softness, strength) theory. The procedures to be employed for the introduction of strength have never been clearly elucidated.[3] The qualitative rationalization of results with HSAB can either work or not work. If it does not work, the failure can be attributed to strength. Thus, one can never miss, but, alas, the whole approach can never be tested. Since there is no chance ever to fail or to test the approach, there is no way to determine if any of this corresponds to reality. This apparent advantage for after the fact rationalization devastates the predictive power of the theory. Since we have not been provided with tables of strength, how can we predict anything? In qualitative use, how do we know the relative importance of hardness and softness *vs.* strength, *i.e.*, when do we know which one to use or ignore? Furthermore, if one reads all of the quantum mechanical explanations of hardness and softness, one wonders what is left over to give an enthalpy contribution for this term called strength. Since hardness and softness as employed in HSAB have a magnitude, there is some strength of bonding associated with these effects.

Again, since the matter has never been clearly defined, it is difficult to see how Pearson's quantitative statement[2] of HSAB can possibly work. Since we have not been told how this quantitative statement is to work, we must examine all possibilities to see if it will. If we substitute $-\Delta H$ for $\log K$ (these terms are used interchangeably in HSAB), we can write his equation as

$$-\Delta H = S_A S_B + \sigma_A \sigma_B \tag{2}$$

where "$\sigma_A \sigma_B$ is hardness or softness."[2] An equation of this form must fit the enthalpy data as well as our *E* and *C* equation

$$-\Delta H = C_A C_B + E_A E_B \tag{3}$$

However, can parameters be found for eq 2 which are *consistent with our qualitative intuition about hardness, softness, and strength*? The equalities recently made,[2] $C_A = \sigma_A$, $C_B = \sigma_B$, $E_A = S_A$, and $E_B = S_B$, are surely incorrect. The $(C_2H_5)_2S$-I_2 adduct would have a large softness contribution and work well, but everything we view as being mainly electrostatic, *e.g.*, $(C_2H_5)_2O$-C_6H_5OH, would have to

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(1) R. S. Drago and R. A. Kabler, *Inorg. Chem.*, 11, 3144 (1972).

(2) R. G. Pearson, *Inorg. Chem.*, 11, 3146 (1972).

(2a) Note Added in Proof. The equation

$$-\Delta H = H_A H_B + (K - H_A)H_B + (K' - H_B)H_A + (K - H_A)(K' - H_B)$$

reduces to $\Delta H = KK'$ and obviously will not work. The equation

$$-\Delta H = H_A H_B + H_A \frac{1}{H_B} + H_B \frac{1}{H_A} + \frac{1}{H_A}\,\frac{1}{H_B}$$

does not work significantly better than those reported in ref 1.

(3) R. G. Pearson, *J. Chem. Educ.*, 45, 585 (1968).